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(57) Abstract

The present invention provides inverse hexagonal phase-forming lyotropic liquid crystalline monomers having the formula (I): HG^1–$T(X^1$–$PG^1)_n$, in which HG^1 represents a "hydrophilic" head group; T represents a bond or a template for the attachment of lipid tail groups, the template being an aromatic ring, monosaccharide, or polyhydroxylated lower alkyl group; each X^1 independently represents a hydrophobic lipid tail group in a linear or branched chain and optionally interrupted by one or more heteroatom groups and wherein R is alkyl or group; each PG^1 is a polymerizable group; and n is an integer from 1 to 4. The present invention also provides an ordered nanocomposite and a method for synthesizing the same. The composite has a matrix component and a filler component. In other aspects, the present invention provides a nanoporous, hexagonal polymer network which is useful for catalysis of chemical reactions and for the purification of solutions including both liquids and gases using membrane filtration.

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NANOCOMPOSITES, NANOPOROUS POLYMER MEMBRANES AND CATALYSTS

BACKGROUND OF THE INVENTION

Nanometer-scale architecture is frequently encountered in biological structural materials and is largely responsible for their impressive properties. See, Addadi, *et al.*, *Angew. Chem. Int. Ed. Engl.* **31:**153 (1992). Bone, for example, is comprised of 4 nm thick hydroxyapatite crystals grown within a regular collagen matrix. See, Heuer, *et al.*, *Science* **255:**1098 (1992); and Katz, *et al.*, *Conn. Tissue Res.* **21:**149 (1989). The construction of synthetic nanocomposites and materials with nanometer-scale domains has received considerable attention due in part to the desire to synthesize analogs to biological materials. See, Mark, *et al.*, *Mater. Sci. Eng.* **C1:**159 (1994). Such nanocomposites are expected to possess unique properties similar to their biological counterparts as a result of their sophisticated nanoarchitectures.

Conventional processing techniques have been unable to achieve nanometer-scale architectural control in the fabrication of bulk, man-made materials. Thus, one of the goals in materials chemistry has been the development of methods for constructing synthetic composites with a degree of nanometer-scale organization similar to that in biological systems while retaining the ability to incorporate modern engineering materials. See, Heuer, *et al.*, *ibid.* and Mark, *et al.*, *ibid.* Several methods have recently been developed for controlling architecture and inducing anisotropy on the small scale in the design of synthetic organic-inorganic composites. For example, elongated ceramic particles have been precipitated within polymer matrices by drawing the polymer during the precipitation reaction (see Burdon, J.; Calvert, P. In *Hierachially Structured Materials*); silica (see, Kovar, R. F.; Lusignea, R. W., In *Ultrastructure Processing of Advanced Ceramics*) and CdS (see, Nelson, *et al.*,

Mater. Sci. Eng. **C2**:133 (1995)) have been precipitated in liquid-crystalline polymers; metals have been electrodeposited inside the pores of commercial nanopore membranes (see, Martin, *Chem. Mater.* **8**:1739 (1996)); and polymers have been grown within the cavities of layered inorganic structures (see, Okada, *et al.*, *Mater. Sci. Eng. C* **C3(2)**:109 (1995)) and zeolites (see, Frisch, *et al.*, *Chem. Mater.* **8**:1735 (1996)). More recently, an organic-inorganic nanocomposite was formed by dissolving the inorganic polymer $(LiMo_3Se_3)_n$ in a conventional monomer acting as the solvent and then polymerizing the matrix *in situ*. See, Golden, *et al.*, *Science* **273**:5276 (1996). However, none of these methods are versatile enough to offer good control over both nanometer-scale architecture and chemical composition for the facile synthesis of bulk materials.

What is needed in the art are new versatile strategies for constructing ordered nanocomposites with well-defined tuneable nano-architectures and the ability to incorporate a wide variety of filler materials. The present invention provides such methods as well as nanometer-scale composite materials and nanoporous polymer matrixes suitable for filtration and catalysis.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides polymerizable, inverse hexagonal phase-forming lyotropic liquid crystalline monomers having the formula:

$$HG^1\text{—}T(X^1\text{—}PG^1)_n \qquad \text{(I)}$$

in which HG^1 represents a "hydrophilic" head group; T represents a bond or a template for the attachment of lipid tail groups, the template being an aromatic ring, monosaccharide, or polyhydroxylated lower alkyl group; each X^1 independently represents a hydrophobic lipid tail group having from 8 to 24 carbon atoms in a linear or branched chain and optionally interrupted by one or more heteroatom groups which can be —O—, —NH—, —NR—, and —S— wherein R is a lower alkyl or

lower acyl group; each PG^1 is a polymerizable group; and n is an integer from 1 to 4.

In another aspect, the present invention provides a matrix component which is formed by the polymerization of inverse hexagonal phase-forming lyotropic liquid-crystalline monomers.

In still another aspect, the present invention provides an ordered nanocomposite. The composite has a matrix component and a filler component. The matrix component is a first material that defines tubular hexagonally-packed channels and is prepared by the polymerization of inverse hexagonal phase-forming lyotropic liquid-crystalline monomers. The filler component is a second material which can be reacted or polymerized into a solid or semi-solid form to fill the tubular hexagonally-packed channels.

In yet another aspect, the present invention provides a nanoporous, hexagonal polymer network which is useful for catalysis of chemical reactions and filtration of solutions and gases. The nanoporous polymer comprises polymerized inverse hexagonal phase-forming lyotropic liquid-crystalline monomers and defines a hexagonally packed array of tubular channels. Optionally, the matrix of polymerized inverse hexagonal phase-forming monomers is prepared by polymerization of the monomers in the presence of crosslinkers. These nanoporous polymers can be formed into a variety of structures including fibers, crystalline-type solids and membranes.

In other aspects, the present invention provides (1) methods for catalyzing chemical reactions by conducting those reactions in the presence of nanoporous polymers described herein and (2) methods for the purification of solutions including both liquids and gases using membrane filtration wherein the membranes are formed from the nanoporous polymer networks described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the broad concept of the nanocomposites of the present invention.

Figures 2a, 2b, and 2c illustrate the structural motifs for a hexagonal, lamellar, and inverse hexagonal phase-forming liquid-crystalline monomers, respectively.

Figure 3 illustrates an x-ray diffraction profile of a polymerized mixture which exhibits x-ray diffraction *d* spacings with ratios of $1 : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{7}} : \frac{1}{\sqrt{9}} : \frac{1}{\sqrt{12}} \ldots$ indicative of a hexagonal phase.

Figure 4 illustrates ^{29}Si solid-state NMR spectra of a silica-containing nanocomposite which was used to verify the extent of condensation of tetraethylorthosilcate (TEOS) within the matrix.

Figure 5a and 5b illustrate the optical texture under crossed polarizers and the x-ray diffraction profile of a nanocomposite which is essentially identical to that of the liquid-crystalline monomer mixture used to prepare the matrix.

DETAILED DESCRIPTION OF THE INVENTION

Abbreviations and Definitions

As used herein, the term "composite" refers to a material composed of two or more distinct components. The components are present as a continuous matrix and a reinforcing structure. A composite is formed when two or more materials are combined with the intent of achieving better properties than can be achieved with a single, homogeneous material. The term "nanocomposite" refers to a composite in which the reinforcing structure has regular dimensions on the nanometer-scale (*e.g.*, 1 to 20 nanometer diameter rods).

As used herein, the term "critical packing parameter" refers to a value defined as the ratio of the volume occupied by the tail(s) of an amphiphilic molecule, divided by the product of the tail length and head group area.

The term "liquid-crystalline" refers to having fluid properties similar to that of a viscous liquid and a degree of molecular order reminiscent of a crystalline solid.

As used herein, the term "lyotropic liquid-crystalline monomers" refers to polymerizable amphiphilic molecules that

spontaneously self-assemble into fluid, yet highly ordered, matrices with regular geometries of nanometer-scale dimension. As used in the present invention, the lyotropic liquid-crystalline monomers are used to form an inverse hexagonal phase around hydrophilic solutions containing, for example, precursors to inorganic solid state materials or organic polymers.

General

The present invention provides new composite materials and methods for the synthesis of composite materials with architectural control on the nanometer scale. The broad concept of the invention is illustrated in Figure 1.

The nanocomposites of Figure 1 are prepared by first forming an inverse hexagonal phase consisting of a suitable unpolymerized yet polymerizable lyotropic liquid-crystalline monomer(11)in the presence of a solution containing reactive agents. Polymerization of the lytropic liquid-crystalline monomers serves to lock in the matrix architecture 12 which consists of a rigid framework of a crosslinked matrix 13 defining hexagonally packed tubular channels 14. Chemical reactions can then be performed within the hexagonally packed channels 14 to form a solidified channel filler 15 in the channels and thereby yield the final composite material 16.

Thus, in one aspect, the present invention provides an ordered nanocomposite. The composite has a matrix component and a filler component. The matrix component is a first material that defines tubular hexagonally-packed channels and is prepared by the polymerization of inverse hexagonal-forming lyotropic liquid-crystalline monomers. The filler component is a second material which can be reacted or polymerized into a solid or semi-solid form to fill the tubular hexagonally-packed channels.

The lyotropic liquid-crystalline monomer system acts as an organic template, providing the underlying order of the composite system. Polymerization of the template, optionally in the presence of a cross-linking agent, with retention of

the liquid-crystalline order can be confirmed using low-angle x-ray diffraction spectroscopy and polarized light microscopy. Subsequent initiation of chemistry within the resulting, ordered hydrophilic domains yields an anisotropic nanocomposite.

The nanocomposites of this invention are formed by the polymerization of inverse hexagonal phase-forming monomers. The polymerization is optionally carried out in the presence of a crosslinker to add greater structural integrity to the composite matrix. Additionally, the polymerization is carried out in a solution which contains reactive precursors to a channel filler material. The precursors can be selected to provide a variety of properties to the composite. Depending on the nature of the precursor materials, the channel filler component will be formed during the polymerization of the matrix, or alternatively, after the matrix has been formed.

I. Inverse Hexagonal Phase-Forming Monomers

The lyotropic liquid-crystalline monomers which are useful for forming the composites and matrices of the present invention are inverse hexagonal phase-forming monomers. These monomers will spontaneously self-assemble into fluid yet highly ordered matrices with inverse hexagonal phase geometries as depicted in Figure 2. The term "inverse hexagonal phase" describes the matrix geometry of the tubular channels in which the hydrophilic head groups of the monomers are orientated toward the center of the cylinder axis and the hydrophobic tail portions extend outward. Confirmation of the inverse hexagonal geometry can be made by polarized light spectroscopy or low angle x-ray diffraction.

These monomers will form different three-dimensional arrays (or "phases") depending on the critical packing parameter of the monomer. The three possible phases are hexagonal 21 (Figure 2a), lamellar 22 (Figure 2b),and inverse hexagonal 23 (Figure 2c, which is the subject of this invention). The critical packing parameter is a function of the effective area of space occupied by the hydrophilic head

group (e.g., a phosphatidylcholine group) and the length of the lipid tail, relative to the volume of space occupied by the lipid tail group. Normal hexagonal phases 21 (Figure 2a) are formed from monomers in which the volume of space occupied by the polar head group is larger than that occupied by the tail group. Because of this aspect ratio, hexagonal phase monomers will assemble into hexagonally packed cylindrical arrays in which the hydrophobic tail groups 26 occupy the center of each cylinder and hydrophilic head group 27 form the periphery, the cylinders themselves surrounded by water 28. Lamellar phases 22 (Figure 2b) are found in liposomes and are formed by monomers such as phospholipids whose critical packing parameter is about 1. In lamellar phases, the layers of organic solution 24 alternate with layers of water 25.

Inverse hexagonal phases 23 (Figure 2c), which are the subject of this invention, are formed from monomers in which the volume of space occupied by the hydrophilic tail group is larger than the volume of space occupied by the polar head group. Because of this aspect ratio, inverse hexagonal phase-forming monomers will spontaneously assemble into hexagonally packed tubular channels in which the hydrophilic head groups 29 are oriented toward the center of the tube or cylinder axis and the hydrophobic tail portions 30 extend outward. As a result, water 31 will reside in the centers of the cylinders and the organic solution 32 will reside outside the cylinders. Amphiphiles that are inverse hexagonal phase-forming monomers will typically have some branching in the hydrophobic tail group. In preferred embodiments, the inverse hexagonal phase-forming monomers will have a critical packing parameter that is greater than 2.

One group of inverse hexagonal phase-forming monomers which are useful in the present invention are those monomers having the formula:

$$HG^1-T-(X^1-PG^1)_n \qquad (I)$$

In this formula, HG^1 represents a hydrophilic head group, preferably a charged hydrophilic head group. The letter T represents a bond or a template for the attachment of lipid tail groups. Suitable templates include, for example,

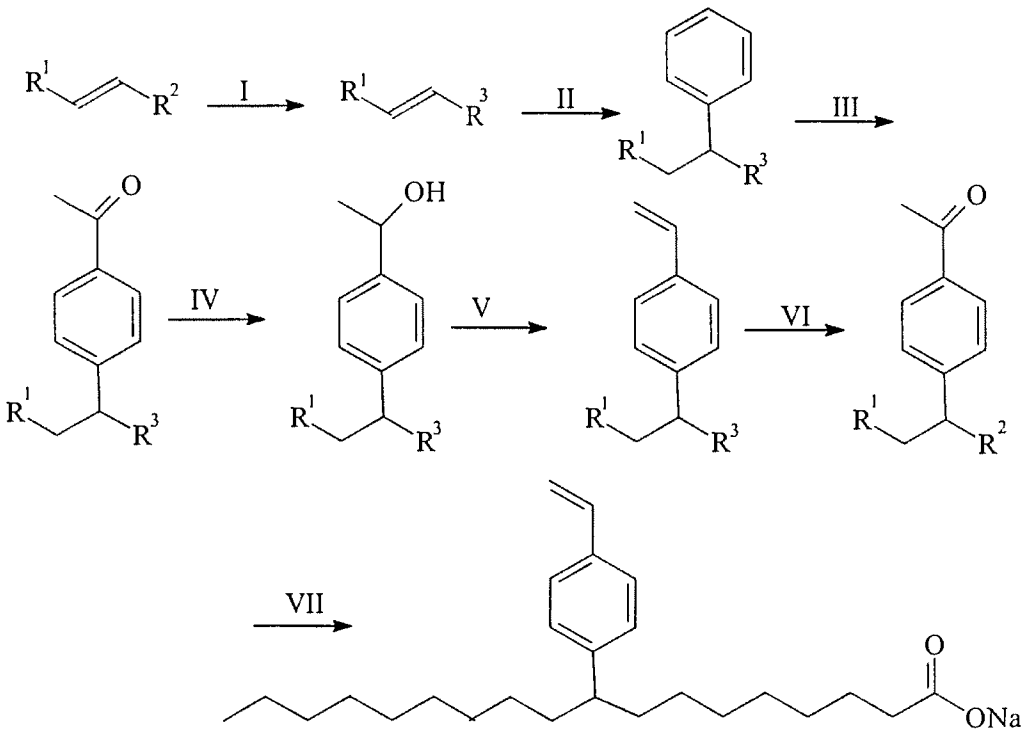
aromatic rings, monosaccharides, and polyhydroxylated lower alkyl groups. Attached to either T or HG^1 (when T is a bond) are X^1 groups which are the same or different from each other and independently represent a lipid tail group having from 8 to 24 carbon atoms in a linear or branched chain, optionally interrupted by one or more heteroatom groups such as —O—, —NH—, —NR—, and —S— wherein R is a lower alkyl or lower acyl group. Each PG^1 is hydrogen or a polymerizable group, preferably a polymerizable group. Examples of suitable polymerizable groups are those which will undergo radically initiated polymerizations such as acrylates, methacrylates, acrylonitrile, methacrylonitrile, ethylenes, styrenes (including α-methyl styrenes), halogenated olefins, vinyl esters, 1,3-dienes, acrylamides, methacrylamides, N-vinyl carbazoles, and N-vinyl pyrrolidines. Preferably, the polymerizable groups are acrylates, methacrylates, acrylonitrile, methacrylonitrile, styrenes (including α-methyl styrenes), vinyl esters, 1,3-dienes, and acrylamides. In the above formula, the letter n represents an integer of from 1 to 4. When n is greater than 1, each X^1 and PG^1 can be independent of the others. For example, when n is 3, each of the X^1 groups can be different and each PG^1 will be independently a hydrogen or polymerizable group. Preferably at least two of the three PG^1 groups are polymerizable groups.

The preparation of two representative inverse hexagonal phase-forming monomers is depicted in Schemes I and II, with experimental conditions provided in the examples below. In Scheme I, a monomer is prepared having the formula above in which T is a bond. The polar head group, HG^1, is a sodium carboxylate salt ($-CO_2^-$ Na^+). Additionally, X^1 is a long chain alkyl group (heptadecyl straight chain) and PG^1 is a *p*-styryl group which is attached to the X^1 chain at a position which provides branching and results in an inverse hexagonal phase-forming monomer. According to the synthesis in Scheme I, the hydrophobic chain of the monomer can be "branched" by the addition of a polymerizable group (or precursor to a polymerizable group) at a non-terminal carbon atom of the chain. The target 1 monomer is a polymerizable styrene analog

of lithium stearate, a molecule which is known to adopt the inverse hexagonal phase.

The monomer is prepared from the Friedel-Crafts reaction of benzene with methyl oleate, generating a mixture of regio-isomers. Acylation of the phenyl ring with acetyl chloride, reduction of the ketone to the corresponding, benzyl alcohol, and dehydration forms the styryl moiety. Saponification of the styryloctadecanoate ester, followed by neutralization with sodium hydroxide, yields the desired monomer.

Scheme I



1

I. MeOH, TSOH, (87%)
II.Benzene, $AlCl_3$ Δ (46%)
III. Acetyl chloride $AlCl_3$ Δ (67%)
IV. $NaBH_4$
V. Fused $KHSO_4$ Δ (55%)
VI. KOH (98%)
VII. NaOH (98%)
R^1= $CH_3(CH_2)_7$-
R^2= -$(CH_2)_7COOH$
R^3=-$(CH_2)_7COOMe$

Initial phase characterization studies revealed that mixtures of this monomer containing small amounts of a crosslinker (ca. 5-10 wt %), an organic photoinitiator (ca. 2 wt %), and water (2-20 wt %) form a well-defined inverse hexagonal phase, as confirmed by polarized light microscopy and low angle x-ray diffraction. The optical textures of these mixtures are consistent with those of other hexagonal phases encountered in the literature.

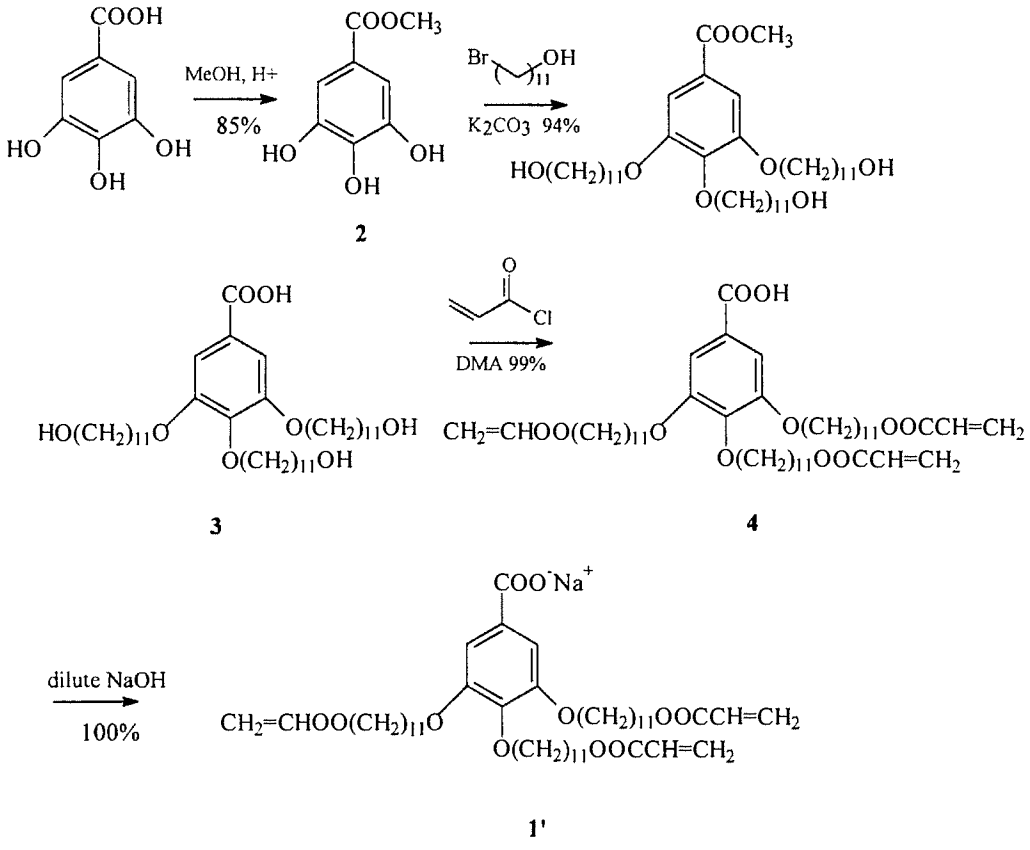
Analogs related to the monomer shown in Scheme I can be prepared by methods well known to one of skill in the art. In particular, other suitable starting materials (unsaturated fatty acids) could be used in place of methyl oleate. Additionally, an olefin moiety present in the unsaturated fatty acid starting material can be derivatized to add functional groups such as hydroxyl groups, amino groups and the like, by methods known by those skilled in the art. Suitable polymerizable groups other than styrene can then be attached to the added functional groups to provide monomers according to the formula above.

Scheme II illustrates the preparation of a monomer in which T is a template for the attachment of lipid tail groups. More particularly, the template is an aromatic ring (*e.g.*, phenyl) having three hydroxyl groups attached at the 3-, 4- and 5-positions of the ring relative to the head group. The polar head group, HG^1, is a carboxylate salt ($-CO_2^-$ Na^+). X^1 is a long chain alkyl group (undecyl straight chain) which terminates in a hydroxy group for the attachment of polymerizable groups. In this instance, the polymerizable groups (PG^1) are each an acrylate group. The preparation of this monomer begins by coupling methyl gallate (2) with three equivalents of 11-bromoundecan-1-ol to form the basic platform of the amphiphile. Saponification of the ester to generate the acid (3), followed by acrylation of the terminal hydroxy groups generates the acid form of the desired monomer (4). Neutralization with NaOH affords pure monomer as the sodium salt (1').

As above, application of standard synthetic methods can be used to prepare other monomers according to the formula.

For example, other templates for the attachment of lipid tail groups can be used such as monosaccharides and

SCHEME II



polyhydroxylated lower alkyl groups (*e.g.*, glycols, 1,2,4-butanetriol). Still other templates can be used provided appropriate functionality is present for the attachment of lipid tail groups. Other examples include spermine and spermidine which have multiple amino groups. Reaction of amino groups with fatty acid alkyl groups terminating in isocyanate, isothiocyanate, and acid chloride groups provides covalent attachment of the lipid tail groups through urea, thiourea, and amide linkages. Alternatively, the amine groups can also be reacted with ω-haloalkanols (*e.g.*, 11-bromoundecanol and related bromoalcohols) to introduce lipid

tail groups having functionality for the attachment of polymerizable groups.

As noted above, suitable polymerizable groups are those which can be polymerized via radical-induced processes. Examples of such groups include acrylates, methacrylates, acrylonitrile, methacrylonitrile, styrenes (including α-methyl styrenes), vinyl esters, 1,3-dienes, and acrylamides. One of skill in the art will understand that appropriate selection of a polymerizable group will be governed primarily by synthesis considerations. For example, lipid tail groups which contain a hydroxyl group for the attachment of polymerizable groups can be reacted with acryloyl chloride or methacryloyl chloride to attach acrylate and methacrylate groups, respectively. Alternatively, the hydroxyl groups can be derivatized to append a styrene moiety via acylation with 4-vinylbenzoic acid or alkylation with vinylbenzylchloride. Similarly, reaction of acryloyl chloride or methacryloyl chloride with a polyamine template (*e.g.*, spermine or spermidine) will result in covalent attachment of acryl and methacryl groups to produce acrylamides and methacrylamides.

Once the monomers have been prepared, evaluation for the formation of an inverse hexagonal phase can be accomplished by standard methods. Typically, a mixture of 80 wt % of the monomer, 10 wt % of an aqueous solution, and 10 wt % of a organic solution containing a photoinitiator, can be examined for the formation of a well-defined, stable inverse hexagonal phase at ambient temperature. The optical texture of this mixture under the polarized light microscope indicates a lyotropic inverse hexagonal mesophase. The x-ray diffraction profile of the polymerized mixture should exhibit *d* spacings with ratios of $1 : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{7}} : \frac{1}{\sqrt{9}} : \frac{1}{\sqrt{12}} \ldots$ indicative of a hexagonal phase (Figure 3). These peaks correspond to the d_{100}, (33) d_{110}, (34) d_{200}, (35) ... diffraction spacings or planes, respectively. In the hexagonal unit cell the interchannel spacing is equal to $d_{100/\cos 30^\circ}$ (36). A trigonal unit cell is defined by 120° (37). Up to about 20 wt % aqueous solution

can usually be incorporated with retention of the inverse hexagonal architecture.

II. Channel Fillers

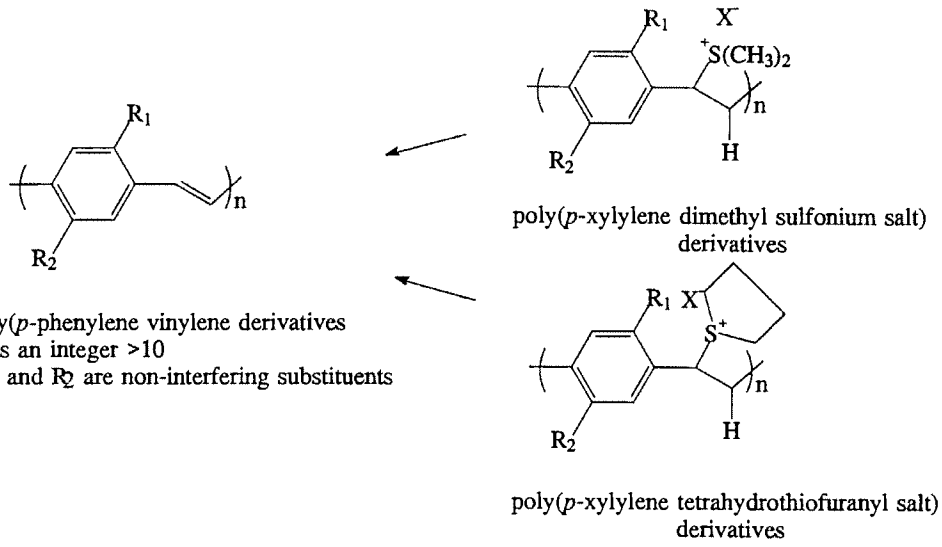
For some of the composites described herein, the hexagonally packed tubular channels are filled with reagents which can provide further structural integrity to the nanocomposite. Alternatively, some channel fillers will provide other properties, such as photoluminescence. The channel fillers will typically be present as precursor materials during the formation of the matrix. Once the matrix is established, the channel filler monomers or reactants can be converted to a component which lends structural integrity to the composite or other beneficial properties. Alternatively, the channel filler monomers can be polymerized coincidentally with the polymerization of the inverse hexagonal phase monomers. A variety of channel fillers are useful for the formation of the present nanocomposites.

In one group of embodiments, the channels fillers are compositions which add structural integrity to the composite. Illustrative of such fillers is sol-gel silica which is prepared from a solution of tetraethylorthosilcate (TEOS). Other sol-gel glasses are also useful such as alumino-phosphates, alumino-silicates, or zirconia-, chromium- or titanium-silicates. Still other channel fillers or precursor materials would include magnetic ceramic particles or alumina.

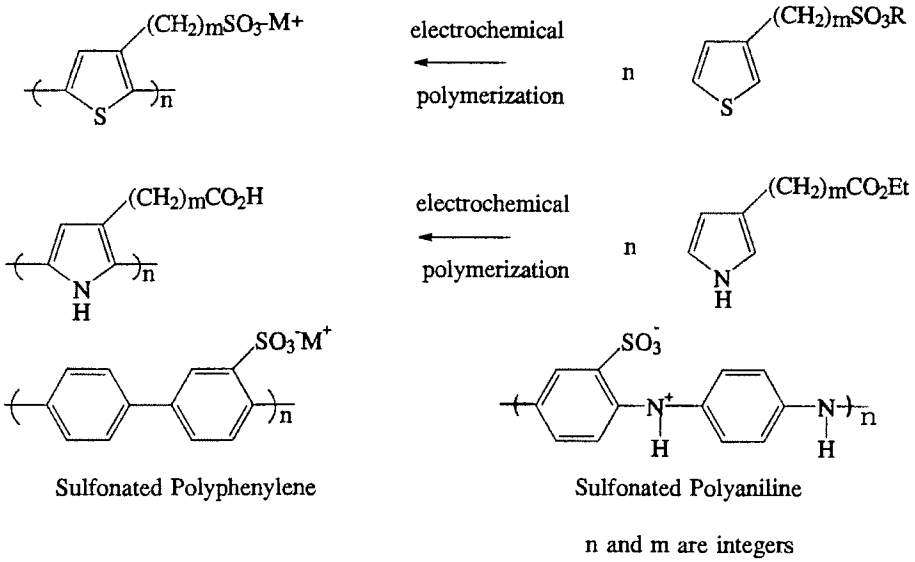
In another group of embodiments, the channels fillers are compositions which add other beneficial properties to the composite. Illustrative of such fillers are semiconductors, metal salts, metal particles, and conjugated organic polymers. A variety of organic semiconductors can be utilized as channel fillers and can be prepared from such precursors as poly(*p*-xylylenetetrahydrothiofuranyl salts) or poly(*p*-xylylene-dimethylsulfonium salt) derivatives (see Scheme III). The organic semiconducting polymers are insoluble in aqueous based solutions and must be formed in the channels from soluble precursors. Metal salts useful as channel fillers will include semiconductors (*e.g.*, CdS, TiO_2, Cu_2S, HgS, CdSe, ZnS, PdS and In_2S_3), magnetic particles (*e.g.*, Fe_3O_4), and

Scheme III

ORGANIC SEMICONDUCTING POLYMERS



WATER-SOLUBLE CONJUGATED POLYMERS



reinforcing salts (*e.g.*, Ag_2O, Fe_2O_3, $Ca_3(PO_4)_2$, $CaCO_3$, $CaSO_4$, and CuO). Metal particles which can be used as channel fillers are those which are suitable for catalyzing certain organic reactions and will include, for example, Pt, Pd, Rh,

Ir and Au. Deposition of these metal particles in a channel can be accomplished by photolysis of soluble precursor species.

In still other embodiments, a series of water-soluble conjugated polymers can be incorporated into the channels during formation of the matrix. As the polymers are water-soluble, no additional conversion to channel filler materials is necessary. Examples of water-soluble conjugated polymers include sulfonated polythiophene, carboxylated polypyrrole, sulfonated polyphenylene, and sulfonated polyaniline (see Scheme III).

III. Methods of Preparing Nanocomposites

In another aspect, the present invention provides methods of forming an ordered nanocomposite matrix comprising polymerized inverse hexagonal-forming lyotropic liquid-crystalline monomers and having hexagonally-packed tubular channels. These methods comprise:

(a) combining a quantity of polymerizable inverse hexagonal-forming monomers, an aqueous or polar organic solvent, and channel filler precursor materials to form a pre-polymer mixture in which the polymerizable monomers spontaneously adopt an inverse hexagonal phase around the aqueous or polar organic solution; and

(b) polymerizing the pre-polymer mixture to form the nanocomposite matrix having hexagonally-packed tubular channels. The channels formed are filled with the aqueous or polar organic solution containing the channel filler precursor materials.

Accordingly, in one group of embodiments, the present inventive methods will further comprise:

(c) reacting the channel filler precursor materials to provide channel fillers.

The inverse hexagonal-forming monomers which are useful in this aspect of the invention are those which have been described above. These monomers can be combined with an aqueous or polar organic solution and channel filler precursor

materials to form a pre-polymer mixture. The order in which the monomers, solvent, and precursors are combined can vary.

Solvents which are useful in the present inventive methods include water, polar organic solvents and combinations thereof. Examples of suitable polar organic solvents include acetonitrile, dimethylformamide (DMF), dimethylsulfoxide (DMSO), sulfolane, dimethylacetamide, 1-methyl-2-pyrrolidinone, and tetrahydrofuran (THF). Preferably, the polar organic solvent is acetonitrile or THF.

The channel filler precursor materials are essentially those which have been described above.

As noted, additional components (*e.g.*, crosslinkers and radical initiators) can be present in the pre-polymer mixture. The use of a crosslinker is preferred for those embodiments in which the inverse hexagonal phase-forming monomer contains a single polymerizable group. A number of crosslinkers are useful in the present invention and include divinylbenzene, N,N-bis-acrylamide, ethylene glycol dimethacrylate, and ethylene glycol diacrylate.

In order to facilitate the polymerization processes which form the matrix and, in some embodiments, the channel filler, a radical initiator will optionally be present in the pre-polymer mixture. Suitable radical initiators are those which will form radical species upon exposure to light or heat. Examples of radical photoinitiators include 2-hydroxy-2-methylpropiophenone, 2,2-dimethoxy-2-2-phenylacetophenone, 4,4'-dihydroxy benzophenone. Suitable initiators which are heat activated include essentially any organic peroxide or azo compound (*e.g.*, benzoyl peroxide, azobis(isobutyronitrile), and *t*-butylperoxide).

The quantities of each of the components should be amounts which will not disrupt or interfere with the ability of the inverse hexagonal-forming monomers to adopt an inverse hexagonal phase around the aqueous or polar organic solutions. The amount of each component will vary if additional components, for example, crosslinkers and radical initiators, are added to or otherwise present in the pre-polymer mixture. Typically, the amount of inverse hexagonal-forming monomers in

the pre-polymer mixture will be on the order of 60 to 95 weight % (wt%), preferably about 70 to 90 wt%, more preferably about 75 to 85 wt%.

Amounts of the aqueous or polar organic solutions will typically be about 5 to about 20 wt%, preferably about 7 to about 15 wt%. The aqueous or polar organic solution will optionally contain an amount of a channel filler precursor material which is sufficient to produce the desired nanocomposite. In one group of embodiments, an aqueous solution is prepared containing from 0.1 to 10 wt% (relative to the aqueous solution) of an organic polymer which is a conjugated photoluminescent polymer or a precursor to such a conjugated polymer. Crosslinkers, when present, will typically be present in an amount of from 2 to 30 wt%, preferably about 10 to about 20 wt%. Radical initiators, when present, will typically be present in an amount of from about 0.5 to about 5 wt%, preferably about 1 to 3 wt%.

Once the components of the pre-polymer mixture have been combined and an inverse hexagonal phase has been formed, the matrix architecture can be "locked in" by polymerizing the inverse hexagonal phase-forming monomers. Methods which are useful for initiating the monomer polymerization include both applying light (*e.g.*, ultraviolet light) and heat. Preferably, the polymerization is performed with ultraviolet light of a suitable wavelength either in bulk or in thin films. Confirmation of the inverse hexagonal matrix architecture can be established by polarized light microscopy, transmission electron microscopy, and x-ray diffraction. The polymerized material will typically contain a regular, hexagonal array of channels, each of the channels having a diameter of about 2 to about 10 nanometers. The dimensions of the hexagonal unit cell and the size of the channels can be varied by altering the composition of the pre-polymer mixture or the structure of the liquid-crystalline monomer. In preferred embodiments, the channels have diameters of from about 2 to about 6 nanometers. Components of the pre-polymer mixture which are not polymerized in the formation of the matrix are typically present in the channels as part of an

aqueous or polar organic solution.

Completion of nanocomposite formation is carried out by reacting the channel filler precursor materials to provide channel fillers. Examples of channel fillers have been provided above. Depending on the channel filler precursor materials, the channel filler can be formed by any of the conventional polymerization techniques known to those with skill in the art. For example, polymerization of channel filler precursor materials can be accomplished with acid or base catalysis, heat, light, or combinations thereof. As provided in the examples below, a channel filler precursor material such as TEOS can be polymerized by acid catalysis when the "acid" is present in the channels as a photoacid (*e.g.*, a light-induced acid generator). PPV, poly(p-phenylene vinylene), is formed by using a water-soluble precursor polymer such as poly (*p*-xylylenedimethylsulfonium chloride) as the channel filler precursor material and heating the precursor to yield PPV upon elimination. Ceramic particles and salts can be formed by using a water-soluble solution of the cation to form the initial inverse hexagonal phase, and then diffusing in a gaseous or aqueous reagent to react and form an insoluble filler material in the channels (*e.g.*, 3 Ca^{2+}, 6 Cl^- and 2 K_3PO_4 provides 6 KCl and $Ca_3(PO_4)_2$ as a solid). Metal particles can be deposited by photolyzing or adding reducing agents to appropriate soluble precursors, as described above.

IV. Ordered, Nanoporous Catalysts

Solid catalysts such as zeolites have the advantages of being tunable, recyclable, and easily separated from reaction mixtures. Zeolites are crystalline framework structures with uniform pore systems. The channels facilitate catalysis by providing a high concentration of active sites and localizing the reactants in the pores.

Mesoporous molecular sieves, by contrast are not crystalline. Molecular sieves are generated from a surfactant to form an amorphous glass with no regular three dimensional array. A distinct advantage of mesoporous molecular sieves

over zeolites is the tunability of the pore size which is easily adjustable from about 20 to 100 Å. Varying the pore size permits one to control the selectivity of the catalyst. The catalytic activity of mesoporous sieves has shown promising results in acid, base, and redox catalysis, as well as other catalytic applications

The polymer matrix portion of the nanocomposites described above, combines the tunability of pore size with the channel structure of zeolites. The "polymer matrix portion" is the material that defines tubular hexagonally-packed channels and is prepared by the polymerization of inverse hexagonal-forming lyotropic liquid-crytalline monomers with no filler component present.

Although the polymer matrix is not fully crystalline, the assembly is highly ordered, possesses ionic functionality in the channels, and is processible into films by conventional fabrication techniques. These properties offer distinct advantages over prior art materials and make the ordered organic networks a desirable potential addition to materials with applications in heterogeneous catalysis.

This aspect of the invention provides a solid matrix in which the channel filler precursor materials have not been incorporated into the polymerized matrix. The resulting matrix of polymerized inverse hexagonal phase-forming lyotropic liquid crystalline monomers contains an ordered array of hexagonally packed tubular channels. The "empty" matrices can then be modified to have utility in the same manner as "molecular sieves." More particularly, the channels can be functionalized to provide the matrix with different reactive properties. Their unique chemical and channel structure allows the "empty" matrices to be used to catalyze chemical reactions in much the same way as zeolites and mesoporous sieves are utilized. Example 5 below describes in

detail the use of a nanoporous matrix as a catalyst in the Knoevenagel reaction.

Besides the catalytic reaction shown in the example, other applications of the present technology include condensation reactions of other combinations of carbonyls and activated methylene compounds. Still further, the base catalysis indicated for the Knoevenagel reaction, is not so limited. Other base catalyzed reactions can also be carried out using the polymer matrix described above.

Yet another major area of interest is the performance of the liquid crystal network (polymer matrix) as an acid catalyst. This involves the ion exchange of the Na^+ cation for a proton to make the acid form of the polymer matrix. Two routes exist for the preparation of the acid form: the carboxylic acid of the monomer can be used to form a liquid crystal phase (a method before polymerization) or the polymer matrix can undergo ion exchange after polymerization. Not only are base and acid catalysis feasible, but now applications in redox catalysis are possible when transition-metal and lanthanide ions are ion-exchanged into the channels of the polymer matrix.

In addition, the size selectivity properties of the polymer matrix can also be exploited. In particular, the exclusion or inclusion of certain reactants can be controlled by controlling the pore size of the nanocomposites.

V. Nanoporous Polymer Membranes

Current polymer membrane manufacturing technologies afford extremely poor control over critical structural features such as pore size, pore architecture, and pore density in the size regime of about 10 Å to 1000 nm. In addition, current technologies offer few chemical alternatives to addressing the problems of membrane fouling which degrade membrane performance with use. In the nanoporous polymer membranes of this invention, the arrangement, size, and chemical properties of the pores may be tailored on the

molecular level by using self-assembling, lyotropic liquid-crystalline monomers as building blocks.

An important application of the invention described herein is water purification. Current water purification technologies include distillation techniques, freezing procedures, reverse osmosis, electrodialysis, and nano/ultrafiltration. These processes suffer from problems of separation efficiency and energy efficiency as a direct result of the lack of uniform pore sizes and pore alignments in the membranes themselves. The crux of the problem lies in the availability of viable techniques for adequately controlling architecture on the nanometer-scale for the synthesis of man-made materials, in particular, polymers.

Monomers having the ability to self-organize in the presence of water provide a means of better controlling order and uniformity on the small scale for the construction of porous polymer networks. Additionally, the effects of this small scale organization and uniformity on the bulk membrane separation properties are enhanced. Still further, the polymer networks have uniform pore sizes on the nanometer scale and a technology that allows the arrangement, size, and chemical nature of the pores to be controlled via the rational design of polymerizable liquid-crystalline starting materials.

The present invention provides the use of self-organizing monomers based on lyotropic liquid crystals as a means of constructing highly ordered polymer networks containing functionalized, well-defined pores with uniform sizes and architectures in the nanometer regime. The proposed features and advantages of this technique over existing polymer membrane synthesis technologies are (1) control over pore size in the nanometer regime, (2) attainment of pore size uniformity, (3) the ability to obtain uniform pore channel architecture and alignment over macroscopic areas, and (4) the ability to incorporate different functionalities and alter the chemical nature selectively in the pores.

(a) Polymer Membrane Synthesis

Polymer membrane can be formed from lyotropic amphiphilic liquid crystal monomers that will self-organize into stable, inverse hexagonal phases in the presence of pure water, or other hydrophilic solutions. These matrix monomers will incorporate readily polymerizable groups, such as activated olefins, in their hydrocarbon tails. Since lyotropic liquid crystal phases are known to be tolerant of small amounts of organic additives, it is possible to incorporate a small amount of an organic radical photoinitiator into the hydrophobic regions of the phase Subsequent *in situ* photopolymerization of the hydrophobic tails into a heavily crosslinked network with retention of the template microstructure then yields a robust polymer network with highly uniform pores arranged in a regular hexagonal array, thus affording an extremely high pore density. The water in the pores can then be removed *in vacuo*, extraction with more volatile solvents, or by thermal evaporation if desired.

Polymer membranes can thus be formed from lyotropic monomers with polymerizable groups that will self-assemble into inverse hexagonal phases in the presence of a hydrophilic solution. Subsequent photopolymerization generates a crosslinked network with retention of template microstructure with uniform pores arranged in a regular hexagonal array.

Membrane synthesis in accordance with this invention offers many potential advantages over existing membrane manufacturing techniques. First, the use of designer lyotropic liquid crystal monomers offers the opportunity to not only control the geometry of the liquid crystal matrix but also to tune the dimensions of the internal domains in an extremely uniform manner. It is well known that the type of liquid crystal phase and the dimensions of the internal aqueous domains can be altered by changing such bulk parameters as the ionic strength of the aqueous solution incorporated, the composition of the system (*i.e.*, the presence of additives and co-surfactants), and the temperature of the system. Similar changes in phase architecture can also be accomplished via modifications in the structure of the

liquid crytals themselves, such as altering the tail volume to headgroup area aspect ratio, the nature of the hydrophilic headgroup, and even the nature of the counterion associated with the amphiphile. This dependence on monomer and system design offers incredible versatility for tuning pore size and architecture on the nanometer scale. Second, the ability to use lyotropic liquid crystal monomers containing different hydrophilic headgroups offers the ability to systematically and selectively control the chemical nature of the linings of the pores. This control is a direct result of the fact that lyotropic liquid crystal monomers arrange themselves in their mesophases predictably with all the hydrophilic headgroups encapsulating the aqueous domains (*i.e.*, the pore channels). Thus, a membrane with a high affinity for cations is easily synthesized by the appropriate choice of a negatively charged headgroup in the initial monomer. Similarly, a membrane with high affinity for dissolved anions can be synthesized equally easily by incorporating an appropriate positively charged headgroup. Since an ionic headgroup on the amphiphilic monomer is only required for formation of the initial lyotropic mesophase, it is even possible to chemically modify the headgroups into neutral functional groups and subsequently re-derivatize the pore channel linings after the matrix microstructure has been locked-in by crosslinking. Finally, the natural tendency of lyotropic liquid crystal phases to self-assemble into regions of local order also opens the door for uniformly aligning the pores in these membranes over macroscopic distances. By using appropriate processing techniques on the initial fluid monomer phases, it is possible to obtain the uniform channel alignment over large areas required for high flow rates.

(b) Monomer Design and Synthesis

The development of suitable lyotropic liquid crystal monomers has focused on the design and synthesis of amphiphilic molecules containing a relatively compact ionic headgroup and a branched hydrophobic tail system containing reactive styrene or acrylate end groups. The design and

synthesis of polymerizable amphiphiles containing reactive styrene and acrylate groups are preferred because these groups are the easiest to polymerize via conventional radical initiators. In order to obtain lyotropic liquid crystals that exhibit the inverse hexagonal phase, the molecules must meet certain empirical structural criteria. It has been found the amphiphiles that exhibit the inverse hexagonal lyotropic liquid crystal phase generally have hydrophobic organic tails with a high degree of branching and relatively small ionic headgroups. In fact, a simple formula has been developed for relating the type of lyotropic liquid crystal phase favored as a function of the tail volume (v), critical tail length (l_c), and the headgroup area (a_o) of an amphiphile. Thus, the liquid crystal monomer must be designed so that the aspect ratio of tail size to headgroup size is relatively large in order for the inverse hexagonal phase to be favored (the critical packing parameter must be greater than 1).

(c) Monomer Cross-Linking

Since product **1** in Scheme I contains only one polymerizable group (and thus cannot form a crosslinked network intrinsically), a difunctional crosslinker such as divinylbenzene is preferably incorporated into the organic domains of the mesophase in order to form a stable network. This requirement is, in fact, beneficial to the formation of the desired inverse hexagonal phase, since the incorporation of organic additives is empirically known to favor inverse lyotropic phases.

Monomer **1'** of Scheme II, on the other hand, is a trifunctional monomer that is intrinsically capable of forming a crosslinked network. Monomer **1'** of Scheme II was specifically designed to be easily assembled in a modular fashion in order to accommodate different tails and reactive groups for tuning liquid crystal phase properties in the future. The key to the simple and versatile synthesis of **1'** of Scheme II is that acrylate groups are placed at the ends of the hydrophobic tails. The use of a multi-tailed amphiphile design with terminal polymerizable groups will be able to

avoid phase changes during polymerization and still afford ease of monomer modification.

(d) Monomer Phase Characterization

The lyotropic liquid crystal phases of the monomers are characterized by polarized light microscopy, low angle x-ray diffraction, and transmission electron microscopy (TEM). This combination of techniques revealed that both monomers of Schemes I and II exhibit the desired inverse hexagonal lyotropic liquid crystal mesophase at room temperature in the presence of water. The presence of the inverse hexagonal phase for these monomers was confirmed by low angle x-ray diffraction studies. The *d* spacings observed for typical mixtures of these monomers at room temperature are consistent with the characteristic $1 : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{7}} : \frac{1}{\sqrt{9}} : \frac{1}{\sqrt{12}} \ldots$ spacing ratio for an inverted hexagonal phase.

(e) In Situ Polymerization with Retention of Phase Microstructure

Lock-in polymerization of the lyotropic liquid crystal monomer phases is accomplished by dissolving a small amount of a conventional organic radical photoinitiator into the hydrophobic regions of the phase and then initiating the crosslinking with UV light. Radical polymerization is the preferred method for forming the ordered network because this mode of polymerization is tolerant of water and a wide range of functional groups in contrast to other polymerization systems. Conventional photoinitiation is a preferred initiation technique over thermal initiation because added heat may disrupt the desired monomer liquid crystal phase, since lyotropic liquid crystal phases are sensitive to temperature as well as system composition. FT-IR and/or UV-visible spectroscopy is then used to determine the degree of polymerization of the networks. Retention of the phase microstructure is determined by polarized light microscopy and low angle x-ray diffraction. Example 6 below describes in situ polymerization.

(f) Control Over Pore Size and the Nature of the Pore Linings

Control over pore size and the chemical nature of the pores is achieved by (1) systematically modifying the structure of the monomers, and (2) systematically varying the composition of the initial monomer mixtures, either by varying the concentrations of the various components or by incorporating appropriate co-surfactants or other additives.

Changes in water content or the presence of organic additives in the inverse hexagonal phases of monomers can affect their unit cell parameters. Monomers of Schemes I and II can be systematically tuned by blending various amounts of different monomers into a single phase, or by adding small amounts of commercial ionic co-surfactants such as Aerosol OT which is also known to exhibit the inverse hexagonal phase. The use of solvents other than water for the formation of the initial monomer inverse hexagonal phase also offers another method for altering pore size. The use of polar organic solvents other than water for the formation of the inverse hexagonal lyotropic liquid crystal phase such as ethylene glycol, NMP, dimethyl acetamide, glycerol, *N*-methylformamide, and DMF offers the capability of using different solvents to tune phase behavior.

Additionally, small structural changes can alter the diameter of the aqueous channels while still maintaining the desired inverse hexagonal phase. Simply changing the nature of the positive counterion (*i.e.*, neutralizing the parent acid with a different metal hydroxide) has a profound effect on the unit cell dimensions (and hence pore size) as well as on the overall phase architecture. Changing the counterion of **1** of Scheme I from Na^+ to K^+ to Ca^{2+} changes the phase from inverse hexagonal to a lamellar back to an inverse hexagonal phase, respectively. More importantly though is that going from a Na^+ to Ca^{2+} counterion modulates the d_{100} unit cell dimension from approximately 35 Å to 31 Å with retention of the desired inverse hexagonal phase. Alternatively, transition-metal and lanthanide analogs of the monomers can be obtained by ion-exchange of the Na^+ ion with appropriate transition-metal and lanthanide nitrate or chloride salts.

Another structural parameter which can be manipulated is the ratio of tail to headgroup size (*i.e.*, the critical packing parameter). Changes to this aspect of amphiphile structure can be used to tune pore size within a stable phase, in addition to changing the geometry of the entire phase itself.

Finally, pore size can also be uniformly and systematically tuned in the polymer networks by photopolymerizing the initial liquid crystal monomer mixtures at different temperatures. It is well known that lyotropic liquid crystal phases are sensitive to temperature as well as composition and amphiphile structure. The effect of temperature on phase behavior and unit cell dimensions can be controlled using a programmable oven.

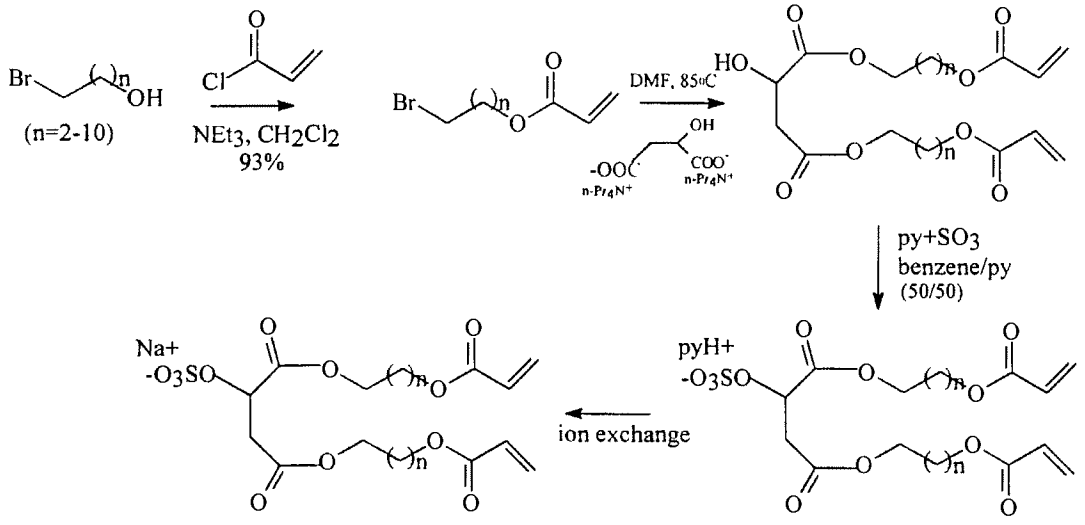
The chemical nature of the pore channels can be controlled by using monomers headgroups specifically selected for particular chemical characteristics. For instance, monomer (**3**) from malic acid has a modular construction as well as the option for incorporating a variety of different headgroups in the final polymer membrane. The synthesis of **3** is shown in Scheme IV. Monomer **3** is also able to incorporate a variety of linear and branched tails via the appropriate bromoalkanol. The advantage of **3** is that the hydroxy group on the bis(tetrapropyl ammonium) malate linker can be derivatized to a variety of ionic groups including the sulfate group. In addition, the sulfate headgroup of **3** can be converted back to a hydroxy group *after* polymerization of the organic matrix using very mild hydrolysis conditions. These pore-localized hydroxy groups may then be converted to a variety of neutral alcohol derivatives by passing the appropriate chemical reagents through the membrane (*e.g.*, acyl halides). This strategy allows us to selectively tune the chemical properties of the pores via chemical functionalization.

(g) Processing and Uniform Alignment of the Pore Channels

Another important consideration for high flux and efficient separation in a porous membrane is the uniform alignment of continuous pore channels.

There is an intrinsic tendency of lyotropic liquid crystal phases to uniformly order on both the local level and the macroscopic level with the aid of external forces. It has been observed that large crystallites of lyotropic liquid crystal phases can be prepared by slow cooling from the melt, annealing by temperature cycling, and applying a low amplitude shear to the phase. Macroscopic alignment of lyotropic liquid crystals can also be achieved by interactions with surfaces, large magnetic fields, or shear. Normal and inverse hexagonal phases are known to form large platelets under the appropriate conditions with the channel axes uniformly aligned parallel (homogeneous orientation) or normal (homeotropic orientation) to glass slides under the microscope. Uniform orientation of these platelets has only been observed over dimensions of 0.1 to 1 cm. By using these techniques for manipulation of the fluid lyotropic liquid crystal monomer phases, large area polymer membranes with the pore channels uniformly normal to the surface of the films can be achieved. Example 7 below describes uniform alignment in the nanoporous polymer membranes.

Scheme IV



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(h) Potential Solutions to Membrane Fouling

One of the pervasive problems with membranes of any composition and design is the problem of fouling. Membranes of all types are susceptible to a decline in flux or rejection characteristics due to the accumulation or deposition of submicron particles on the membrane surface and/or the crystallization and precipitation of smaller solutes on the surface or within the pores of the membrane itself. By designing amphiphilic monomers with a high degree of fluorination in the tails, an ordered nanoporous polymer membrane with low adhesion properties may be made. Partially fluorinated tails can be easily incorporated into monomer **1'** of Scheme II because of its modular design, starting from partially fluorinated linear α,ω-bromoalkanols. To reduce crystallization of minerals within the pores, the chemical nature of the pore linings may also be changed by employing amphiphilic monomers which have a reactive headgroup that can be transformed into a non-ionic organic functional group after membrane polymerization. To increase the stability of these proposed membranes towards basic or acidic aqueous cleaning and operating environments, lyotropic liquid crystal monomers that do not contain weak, hydrolyzable linkages may be employed for maximum chemical inertness.

By the practice of the present invention, pinhole-free, thin films of the inverse hexagonal-phase forming monomers are obtained with the water channels all aligned on average perpendicular to the film surfaces. These films are up to 10 cm in diameter and up to 30 $\pm$ 1 μm thick. This alignment was accomplished by melting the initial lyotropic liquid crystal monomer phase into an isotropic melt between two smooth glass or quartz disks, and then allowing the mixture to slow cool into the aligned inverse hexagonal phase. The aligned phase is then polymerized by UV light into a nanoporous polymer film.

The interchannel spacings (and indirectly the pore sizes) of these films can be uniformly altered from 26 to 41 Å by using analogs of the inverse hexagonal phase forming monomers containing different metal ions on the headgroup. Pore size

control was also found to be possible by altering the length or branching of the flexible tails of the monomer in Scheme II.

EXAMPLES

General

Unless otherwise noted, IR spectra of samples were measured as thin films on NaBr windows using a Perkin-Elmer 1615 series FT-IR spectrometer; the symbols *s*, *m*, *w*, and *br* were used to indicate strong, moderate, weak, and broad absorptions, respectively. All NMR samples of monomer intermediates were prepared using deuterated chloroform as the solvent. All ^{1}H NMR spectra were measured on a Bruker AMX-300 spectrometer; the symbols *s*, *d*, *t*, *q*, and *m* were used to designate singlet, doublet, triplet, quartet, and multiplet signals, respectively. All ^{13}C NMR spectra were measured on a Bruker AMX-400 spectrometer. For intermediates with regioisomers, all resonances are listed. All polarized-light microscopy was conducted on a Leitz DMXRP polarizing, microscope. All low-angle X-ray diffraction studies of liquid-crystalline samples were performed using, an Inel CPS 120 diffractometer, and were verified against a Siemens D-5000 diffractometer.

EXAMPLE 1

This example illustrates the preparation of the lyotropic liquid-crystalline monomer sodium *p*-styryloctadecenoate (*see* 1 in Scheme I).

1.1 Methyl 9-octadecenoate (1)

To a 250-mL round-bottom flask was added 42.0 g (0.149 mmol) of 9-octadecenoic acid and 80 mL of methanol. To the mixture was added 0.761 g (4.00 mmol) of *p*-toluenesulfonic acid. The mixture was heated at reflux under nitrogen for 14 h. The mixture was cooled to room temperature, and the solvents were removed. The crude product was dried over $MgSO_4$. Distillation of the crude product yielded 41.6 g (94.5%) of a clear, viscous liquid, bp 143 °C (35 mtorr). IR: 2922 (s),

2852 (s), 1743 (s, C=O), 1457 (s, $ROCH_3$) cm^{-1}. ^1H NMR (300 MHz): δ 5.33 (m, 2H, cis/trans isomerized), 3.65 (s, 3H, $COOCH_3$), 2.28 (t, 2H, J = 7.2, RCH_2COOCH_3), 1.98 (q, 4H, J = 6.15), 1.57 (quintet, 2H, J = 7.2), 1.25 (m, 20H), 0.88 (t, 3H, J = 6.6 Hz). ^{13}C NMR (101 MHz): δ 174.2 ($RC(=O)CH_3$), [129.9, 129.7] (RCH=CHR), 51.3 ($RC(=O)OCH_3$), 34.0 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 27.2 (CH_2), 27.1 (CH_2), 24.9 (CH_2), 22.6 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{19}H_{36}O_2$: C, 76.97; H, 12.24. Found: C, 76.70; H, 12.12.

1.2 Methyl phenyloctadecanoate (2)

To a 125-mL Schlenk flask was added 19.8 g (0.149 mol) of $AlCl_3$ and 25 mL of freshly distilled benzene. A 100-mL pressure-equalizing addition funnel was attached to the flask under nitrogen flush. To the addition funnel was added a mixture of 30 mL and 41.2 g (0.139 mol) of **1**. The solution of **1** was added to the $AlCl_3$ with stirring at a rate of approximately 1 mL per minute with the temperature moderated by an ice/water bath. The reaction mixture became brown and viscous, and large quantities of HCl gas were evolved. Once HCl gas evolution ceased, the mixture was allowed to stir at room temperature for an hour. The reaction mixture was slowly poured over an ice-chilled 1 M aqueous HCl solution. The product was extracted with diethyl ether (3 × 100 mL). The combined ether extracts were washed with 100 mL saturated NaCl solution and 100 mL deionized water, then dried over $MgSO_4$. Removal of the solvents and distillation of the crude product yielded 29.6 g (56.7%) of a clear, viscous liquid, bp 181 °C (35 mtorr). IR: 2920(s), 2851(s), 1741(s, C=O), 1603 (w, phenyl), 1494 (m, phenyl), [761, 700] (m, monosubstituted phenyl). ^1H NMR (300 MHz): δ 7.31-7.12 (m, 5H, aromatic), 3.67 (overlapping s, 3H, $RC(=O)OCH_3$), 2.48 (m, 1H, RCHPhR), 2.29 (m, 2H, RCH_2COOCH_3), 1.56 (m, 6H), 1.21 (m, 22H), 0.86 (m, 3H, RCH_3). ^{13}C NMR (100 MHz) : δ 174.2 (C=O), [146.3, 146.3, 146.3, 146.2] (Ipso phenyl), [128.2, 128.0, 127.7, 127.6, 127.0, 125.6] (phenyl), 51.5 ($RC(=O)OCH_3$), [47.8, 46.0, 45.7,

39.8, 39.2, 38.4, 36.9, 36.8, 36.7, 36.5, 34.0, 31.9, 31.9, 31.8, 31.7, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 29.2, 29.2, 29.1, 29.1, 29.0, 27.7, 27.6, 27.5, 27.5, 27.4, 27.2, 27.2, 24.9, 24.9, 24.9, 24.8, 22.8, 22.6, 22.6, 22.6, 22.3, 20.9] (CH_2), [14.3, 14.1] (CH_3). Anal. Calcd for $C_{25}H_{42}O_2$: C, 80.16; H, 11.30. Found: cC, 80.00; H, 11.03.

1.3 Methyl *p*-acetylphenyloctadecanoate (3)

(Note: reaction conditions should **not** be rigorously dry.) To a 250-mL round-bottom flask with a sidearm was added 21.3 g (0.160 mol) of $AlCl_3$. A 100 mL pressure-equalizing addition funnel was attached, and 50 mL of nitrobenzene was slowly added to the system. A dark yellow/brown solution formed. To the mixture was added 9.42 g (0.120 mol) of acetyl chloride dissolved in 50 mL of nitrobenzene. A solution of 29.3 g (78.1 mmol) of **2** and 40 mL of nitrobenzene was added dropwise with stirring over a period of 2 h, after which the solution was stirred under N_2 flush for 1 h. The product was pour slowly over ice-chilled 1 M aqueous HCl. The product was extracted with ethyl acetate (3 $^{\times}$ 200 mL). The combined ether extracts were washed with 100 mL saturated NaCl solution and 100 mL deionized water, then dried over $MgSO_4$. Nitrobenzene was removed from the product by distillation under vacuum. Further distillation yielded 25.7 g (78.9%) of a pale yellow liquid, bp 223 °C (80 mtorr). IR: 2923 (s), 2852 (s), 1740 (s, C=O ester), 1684 (s, C=O ketone), 1606 (m, phenyl), 829 (m, para-substituted phenyl). ^{1}H NMR (300 MHz) : δ 7.87 (d, 2H, phenyl para to acetyl, J = 8.4 Hz), 7.20 (d, 2H, phenyl para to alkyl, J = 8.4 Hz), 3.67 (overlapping s, 3H, R(C=O)O**C**H_3), 2.56 (s, 3H, **C**H_3C(=O)Ph), 2.48 (m, 1H, RC**H**PhR), 2.28 (m, 2H, RCH_2COOCH_3), 1.56 (m, 6H), 1.21 (m, 22H), 0.86 (m, 3H, RCH_3). ^{13}C NMR (100 MHz) : δ 197.8 (CH_3**C**(=O)Ph), 174.3 (R**C**OOCH_3), 152.3 (ispo phenyl, alkyl), 135.0 (ipso phenyl, acyl), (128.4, 128.4, 128.2, 127.8, 127.8, 128.1, 125.6] (phenyl), 51.3 (RC(=O)O**C**H_3), [46.1, 46.0, 40.0, 38.0, 36.9, 36.7, 34.0, 31.8, 31.7, 31.6, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.2, 29.1, 27.5, 27.4, 27.3, 26.4, 24.9, 24.8, 22.6, 22.4, 22.0] (CH_2), 14.1 (CH_3). Anal. Calcd for

$C_{27}H_{44}O_3$: C, 77.84; H, 10.64. Found: C, 77.66; H, 10.90.

1.4 Methyl *p*-(1-hydroxyethyl)phenyloctadecanoate (4)

To a 250-mL round-bottom flask were added 25.4 g (61.0 mmol) of **3** and 75 mL of methanol. To a 100-mL flask was added 75 mL of methanol and 2.31 g (61.0 mmol) of $NaBH_4$ slowly with stirring. The $NaBH_4$ solution bubbled readily, and was rapidly transferred to the solution containing **3**. The reaction mixture was allowed to stir for 30 minutes at room temperature. The product was poured over a 1 M aqueous HCl solution, and 150 mL of ethyl acetate were added. The mixture was stirred for 15 minutes at room temperature. The ethyl acetate was isolated, and the HCl solution was extracted with additional ethyl acetate (2 × 50 mL). The combined extracts were washed with 50 mL of saturated aqueous NaCl solution and 50 mL of deionized water. Solvents were removed first by rotary evaporator, then under vacuum. The product, 25.0 g (97.8%) of a viscous yellow liquid, was not distilled so as to prevent polymerization. IR: 3421 (br, -OH), 2925 (s), 2851 (s), 1740 (s, C=O ester), 831 (m, para-substituted phenyl). ^{1}H NMR (300 MHz) : δ [7.28-7.08] (4H, aromatic), 4.85 (q, 1H, $CH_3CH(OH)Ph$, = 6.4 Hz), 3.67 (overlapping, s, 3H, $RC(=O)OCH_3$3), 2.46 (m, 1H, RCHPhR), 2.29 (m, 2H, RCH_2COOCH_3), 1.58 (m, 6H), [1.49, 1.47] (m, 3H, $CH_3CH(OH)Ph$), 1.23 (m, 22H), 0.87 (m, 3H, RCH_3). ^{3}C NMR (100 MHz): δ 174.3 ($RCOOCH_3$), [147.2, 145.6, 145.5, 145.3, 143.1, 143.0] (ispo phenyl), [127.7, 127.6, 127.0, 125.3, 125.2] (phenyl), 70.2 ($CH_3CH_2(-OH)Ph$), 51.3 ($RC(=O)OCH_3$), [47.4, 45.6, 45.4, 39.5, 39.1, 38.4, 36.9, 36.8, 36.6, 36.4, 34.0, 34.0, 31.9, 31.8, 31.8, 31.7, 30.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.5, 29.4, 29.2, 29.2, 29.1, 29.1, 29.0, 28.9, 27.7, 27.6, 27.5, 27.3, 27.2, 27.1, 24.9, 24.7, 22.8, 22.7, 22.61 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{27}H_{44}O_2$: C, 77.46; H, 11.07. Found: C 77.59; H, 11.40.

1.5 **Methyl *p*-styryloctadecanoate (5)**

To a 1-L round-bottom flask were added 24.0 g (57.3 mmol) of **4**, 0.545 g (2.87 mmol) of *p*-toluenesulfonic acid, 0.126 g (0.573 mmol) of BHT, 5 g of 4Å dried molecular sieves, and 400 mL of benzene. The system was heated at reflux for 24 h., after which 5.0 g of $MgSO_4$ and an additional 0.50 g of *p*-toluenesulfonic acid were added. The system was heated at reflux for an additional 24 h. The intermediate product was washed with 200 mL of saturated NaCl solution and dried over $MgSO_4$. The product was purified by column chromatography, yielding 9.01 g (39.2%) of a viscous, pale yellow liquid. bp 213°C (180 mtorr). IR: 2922 (s), 2851 (s), 1741 (s, C=O ester), 1464 (m, ROCH3), [1629, 989, 902] (s, CH_2=CHR), 838 (m, para-substituted phenyl). ^{1}H NMR (300 MHz) : δ [7.35-7.08] (4H, aromatic), 6.70 (1H, CH_2=C**H**R, J_{trans} = 17.55 Hz, J_{cis} = 10.95), 5.71 (1H, $CH_{trans}\mathbf{H}_{cis}$ = CHR, J_{gem} = 0.90 Hz), 5.18 (1H, $C\mathbf{H}_{trans}H_{cis}$=CHR, J_{cis} = 10.95 Hz, J_{gem} = 0.75 Hz), 3.67 (overlapping s, 3H, RC(=0)OCH3), 2.46 (m, 1H, RCHPhR), 2.29 (m, 2H, RC**H**2COOCH$_3$), 1.58 (m, 6H), 1.23 (m, 22H), 0.87 (m, 3H, RC**H**$_3$). ^{3}C NMR (100 MHz) : δ 174.2 (R**C**OOCH$_3$), 146.3 (ispo phenyl, alkyl), 136.8 (CH_2=**C**HPh), 134.8 (ipso phenyl, vinyl), [128.1, 127.8, 127.8, 127.6, 127.0, 126.1, 126.0, 125.6] (phenyl), 112.6 (**C**H_2=CHPh), 51.3 (RC(=O)O**C**H$_3$), [46.0, 45.8, 39.9, 39.2, 38.4, 37.0, 36.5, 34.1, 31.8, 31.7, 30.3, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.2, 29.1, 27.6, 27.4, 26.3, 26.5, 24.9, 22.8, 22.6] (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C 80.79; H, 10.88.

1.6 ***p*-Styryloctadecanoic acid (6)**

In a 100-mL round-bottom flask 0.978 g (24.4 mmol) of NaOH was dissolved in 50 mL of methanol. To this solution was added 8.90 g (22.2 mmol) of **5** dissolved in 25 mL of methanol. The flask was fitted with a condenser, and the solution was heated at reflux for 8 h. The cooled product was poured into a 1 M aqueous HCl solution with stirring. The mixture was extracted with hexanes (3 $^{\times}$ 75 mL), and the combined ether extracts were washed once with 50 mL sat. NaCl

solution and 50 mL deionized water. The resulting product was agitated under vacuum to remove residual hexanes, affording 8.47 g (98.5%) of a viscous, pale-yellow liquid. IR: 3083 (s, br, COOH), 2925 (s), 2854 (s), 1710 (s, C=O), [1630, 989, 902] (s, CH_2=C**H**R), 838 (m, para-substituted phenyl). ^{1}H NMR (300 MHz) : δ [7.35-7.08] (4H, aromatic), 6.71 (1H, CH_2=C**H**R, J_{trans}=17.7 Hz, J_{cis}=10.8), 5.72 (1H, CH*trans***H**$_{cis}$=CHR, J_{trans}= 17.55 Hz, J_{gem}=1.05 Hz), 5.19 (1H, C**H**$_{trans}$H$_{cis}$=CHR, J_{cis}=10.95 Hz, J_{gem}=0.75 Hz), 2.47 (m, 1H, RC**H**PhR), 2.29 (m, 2H, RC**H**$_2$COOCH$_3$), 1.59 (m, 6H), 1.22 (m, 22H), 0.87 (m, 3H, RC**H**$_3$). $_{13}$C NMR (100 MHz) : δ 180.3 (RCOOCH$_3$), [146.4, 146.3, 146.2] (ispo phenyl, alkyl), 136.8 (CH_2=CHPh), 134.8 (ipso phenyl, vinyl), [128.1, 127.8, 127.7, 126.0] (phenyl), 112.6 (CH_2=CHPh), [46.0, 45.8, 37.0, 37.0, 36.9, 34.0, 32.0, 31.9, 31.9, 31.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.0, 28.9, 27.6, 27.5, 27.4, 27.3, 24.6, 24.5, 22.8, 22.7, 22.6, 22.6] (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{26}H_{42}O_2$: C, 80.77; H, 10.95. Found: C 80.63; H, 10.86.

1.7 Sodium *p*-styryloctadecanoate (7)

To a 50-mL round-bottom flask was added 2.50 g (6.47 mmol) of **6** and 10 mL of methanol. A solution of 0.264 (6.60 mmol) of NaOH in 10 mL of methanol was added slowly to the solution of **6**. The solvents were removed under vacuum, leaving behind a pale yellow, sticky solid. IR: 2923 (s), 2851 (s), 1564 (s, C=O), [1630, 988, 902] (s, CH_2=CHR), 838 (m, para-substituted phenyl). ^{1}H NMR (300 MHz, CD_3OD) : δ [7.23-6.96] (4H, aromatic), 6.59 (1H, CH_2=C**H**R, J_{trans}=17.6 Hz, J_{cis}=11-1), 5.60 (1H, CH$_{trans}$**H**$_{cis}$=CHR, J_{trans}=17.4 Hz), 5.04 (1H, C**H**$_{trans}$H$_{cis}$=CHR, J_{cis}=10.8 Hz), 2.36 (m, 1H, RC**H**PhR), 2.03 (m, 2H, RC**H**$_2$COOCH$_3$), 1.45 (m, 6H), 1.13 (m, 22H), 0.87 (m, 3H, RC**H**$_3$). ^{13}C NMR (100 MHZ) : δ 183.2 (R**C**OOCH$_3$), 147.2 (ispo phenyl, alkyl), 138.6 (CH_2=CHPh), 136.9 (ipso phenyl, vinyl), [129.4, 129.0, 128.8, 127.3] (phenyl), 113.1 (CH_2=CHPh), [49.8, 49.6, 49.4, 49.2, 48.9, 48.7, 48.5, 47.1, 39.4, 38.3, 33.2, 31.1, 30.9, 30.9, 30.8, 30.6, 28.8, 28.0, 23.9] (CH_2), 14.7 (CH_3). Anal. Calcd for $C_{26}H_{41}O_2Na$: C, 76.43; H, 10.11. Found: C 75.22; H, 10.24.

EXAMPLE 2

This example illustrates the synthesis of lyotropic liquid-crystalline monomer sodium 3,4,5-tris(11'-acryloyloxyundecyloxy)benzoate (*see* **1'** in Scheme II).

2.1 Methyl-3,4,5-trihydroxybenzoate (2)

3,4,5-trihydroxybenzoic acid (20.00 g, 0.118 mol) is dissolved in 250 mL absolute methanol. Sulfuric acid (2 g, 98%) was added and the solution was refluxed over night (TLC in EtOAc:hexanes=75:25; Rf=2.25 shows quantitative conversion-no starting material present). The solution was neutralized with 10% aqueous NaOH. Excess methanol was removed under reduced pressure and 200 mL of water was added to the residue. The resulting solution was extracted 3 times with portions of 200 mL EtOAc, dried over Na_2SO_4 and filtered over a plug of silica topped with activated carbon. Removal of solvent provided the desired product which is light sensitive. Yield: 18.40 g (84.99%). Elem. Anal. $C_8H_8O_5$, MW = 184.14, calc: C, 52.20; H, 4.40. Found: C, 52.21; H, 4.54. IR: 3421 (O-H), 2928, 2847 (C-H), 1727 (C=O), 1589, 1505, 1340 (C=C, arom), ring breathing, 1436, 1467 $(CH)_2$, scissoring, 1221 C-O-C (alkyl aryl ether stretch), 1128, 1107 $(CH)_2$ twisting, 1059 C-OH (C-O stretching), 933, 897, 861, 764 aromatic substitution pattern, 721 $(CH)_2$ rocking. ^1H NMR: 9.183 (br s, 3H, O-**H**), 6.910 (s, 2H, ar-**H**), 3.700 (s, 3H, CO_2CH_3). ^{13}C NMR: 167.08 (carbonyl), 146.32 (meta, aromatic), 139.14 (para, aromatic), 120.05 (ipso, aromatic), 109.25 (ortho, aromatic), 52.33 (methyl ester).

2.1 3,4,5-Tris(11'-hydroxyundecyloxy)benzoic acid (3)

Methyl 3,4,5-trihydroxybezoate (9.84 g, 0.0534 mol) was dissolved in 250 mL dry DMF. K_2CO_3 (73.80 g, 0.534 mol) was added and the heterogenous mixture was stirred vigorously. The mixture was warmed to 70-80°C and 44.32 g (0.176mol) of 11-bromoundecanol was added slowly. The mixture was stirred for 12 hr at 70-80°C. TLC (EtOAc:hexanes = 50:50) shows complete consumption of bromoundecanol (R_f = 1.6). The

reaction mixture was cooled and the remaining solid was removed. DMF was removed under reduced pressure (Rotavap, 80°C) and water (250 mL) was added. The resulting mixture was extracted with 3 x 200 mL portions of EtOAc. The combined organic phases were dried over Na_2SO_4 and the solvent was removed. The remaining solids were dissolved in 300 mL of a $CH_3OH:H_2O$ = 3:1 mixture containing 56.11 g (0.433 mol) of KOH and heated to reflux overnight. The homogeneous solution was neutralized with 3 M HCl solution and extracted with EtOAc. The combined EtOAc portions were collected and dried over Na_2SO_4 and filtered. The solvent was removed and the solids were recrystallized from EtOAc. Yield: 28.9g (79.5%). Elem. Anal. $C_{40}H_{72}O_8$, MW = 681.1, calc: C, 70.50; H, 10.70. Found: C, 70.28; H, 11.02. IR: 3236.4 (br), 3330.6 O-H, 2918, 2847 C-H, 1680, 1586, 1502, 1330, 1430, 1463, 1221, 1058, 1122, 1210. ^1H NMR: (d_6-DMSO) δ 12.83 (br s, 1H, $RCO_2\mathbf{H}$), 7.15 (s, 2H, ar-**H**), 4.27 (s, 3H, O-**H**), 3.89 (t, 6H, R-C$\mathbf{H}_2$-OH), 1.68 (t, 6H, ar-O-C$\mathbf{H}_2$-R), 1.30 (m, 56H, -C$\mathbf{H}_2$-). ^{13}C NMR (d_6-DMSO): 167.43 (carbonyl), 152.70 (meta, aromatic), 141.51 (aromatic, para), 126.02 (ipso, aromatic), 107.78 (ortho, aromatic), 73.46 ar-O-C$\mathbf{H}_2$-R (para), 69.13 ar-O-C$\mathbf{H}_2$-R (meta), 62.95 R-C$\mathbf{H}_2$-OH, 32.76, 30.30, 29.61, 29.53, 29.48, 29.35, 29.28, 26.04, 25.76 {-(C**H**)$_2$-} x 9

2.3 3,4,5-Tris(11'-acryloyloxyundecyloxy)benzoicacid (4)

3,4,5-Tris(11'-hydroxyundecyloxy)benzoic acid (10 g, 0.0147 mol) was dissolved in 80 mL dioxane and N,N-dimethylaniline (5.88 g, 0.0485 mol) was added. The mixture was warmed to 60°C and 4.39 g (0.0485 mol) of acryloyl chloride were added slowly. The resulting mixture was stirred for 1 hour (rxn complete by TLC) and then 1 mL of CH_3OH was added. The solution was poured into 300 mL of 1.2 M HCl and extracted 3 times with 200 mLl portions of EtOAc. The EtOAc phases were dried over Na_2SO_4 and filtered over a silica plug. The solvent was removed under reduced pressure and the product was recrystallized from EtOAc. Yield: 10.8 g (87.2%). Elem. Anal. $C_{49}H_{78}O_{11}$, MW = 843.15, calc: C, 68.90; H, 9.32. Found: C, 68.91; H, 9.20. IR: 3236.4 (br) RCO2-H, 2918, 2847 C-H,

1723 carbonyl of acrylate, 1684 R(C=O)OH stretch, 1586, 1502, 1331 aromatic ring breathing, 1430, 1467 methylene scissoring, 1408 C=C-H bending (in plane), 1385 RC(=O)-O-H bending, 1271, 1296, 1226 RC(=O)-OH stretch (and RC(=O)-O<acrylate> stretch), 1226 C-C(=O) stretch (for acrylate), 1210 C-O stretch of RCO2H, 1221 alkyl aryl ether stretch, 1125 methylene twisting, 1189 C-C(=O) stretch (for RCO2H), 1062 <acrylate> -O-C-C stretch, 810 C=C-H bending, out of plane. ^{1}H NMR: (D_6-acetone) δ 12.83 (br s, 1H, RCO_2**H**), 7.27 (s, 2H, ar-**H** (ortho)), 6.32 (dd, 3H, CH_2=C**H**-C(=O)OR), 6.13 (dd, 3H, CH_2=CH-C(=O)OR (trans to carbonyl)), 5.86 (dd, 3H, CH_2=CH-C(=O)OR (cis to carbonyl)), 4.18 (t, 6H, CH_2-O-<acrylate>), 4.05 (t, 6H, ar-O-CH_2-R), 1.32 (m, 56H, -CH_2-). ^{13}C NMR (D_6-acetone): 166.44 RCO2H, 165.46 carbonyl of acrylate, 152.89 (aromatic, meta), 129.936 C=CH_2 (of acrylate), 128.718 C(=O)-CH=CH_2, 125.178 (aromatic, ipso), 107.92 (aromatic, ortho), 72.81 ar-O-CH2R (para), 68.75 ar-O-CH2R (meta), 64.10 R-CH2-<acrylate>, 32.76, 30.30, 29.61, 29.53, 29.48, 29.35, 29.28, 26.04, 25.76 {-$(CH)_2$-} x 9.

2.4 Sodium 3,4,5-Tris(11'-acryloyloxyundecyloxy)benzoate (1)

3,4,5-Tris(11'-acryloyloxyundecyloxy)benzoic acid (1.00 g, 0.0011981 mol) was dissolved in 150 mL of tetrahydrofuran. Sodium hydroxide (0.44 g of a 10% NaOH aqueous solution) was then added and the reaction was stirred for 30 min. The solvents were removed *in vacuo* by rotary evaporation. Residual water was removed via azeotrope with 30 mL of acetone under reduced pressure. Yield: 1.02 g (100%). Elem. Anal. $C_{49}H_{77}O_{11}Na$, MW = 864, calc: C, 68.06; H, 8.91. Found: C, 67.31; H, 9.21. IR: 2923, 2851 C-H, 1728 carbonyl stretch, 1637, 1618 C=C stretch, 1576, 1500 aromatic breathing, 1556, 1380 carboxylate, 1467 methylene scissoring, 1122 methylene twisting, 1062 <acrylate>-O-C-C stretch, 1190, 1121 allyl-C(=O) stretch, 1271, 1296 allyl-C(=O)-OR stretch, 1408, 810 C=C-H bending. ^{1}H NMR: δ 7.20 (s, 2H), 6.24 (dd, 3H), 6.10 (dd, 3H), 5.85 (dd, 3H), 4.05 (t, 6H), 3.80 (t, 6H), 1.4 (m, 54H). ^{13}C NMR : 212.60 carboxylate carbon, 165.82

ester carbonyl, 151.77 (aromatic, meta), 131.52 C=CH_2, 128.79 C(=O)-CH=CH_2, 125.306 (aromatic, ipso), 107.25 (aromatic, ortho), 72.60 ar-O-CH_2 (meta), 68.373 ar-O-CH_2 (para), 64.432 R-CH2-<acrylate>, 32.76, 30.30, 29.61, 29.53, 29.48, 29.35, 29.28, 26.04, 25.76 {-$(CH)_2$-} x 9.

EXAMPLE 3

This example illustrates the polymerization of inverse hexagonal-forming lyotropic liquid-crystalline monomers to form matrices having ordered hexagonally-packed tubular channels. Subsequent polymerizations of the channel filler provided the nanocomposites.

3.1 Ordered Nanocomposites from Sodium *p*-styryloctadecenoate as the matrix monomer and a solution of tetraethylorthosilicate as a channel filler

An ordered nanocomposite with hexagonally arranged channels containing silica was synthesized using sodium *p*-styryloctadecanoate (1) as the matrix monomer and a solution of tetraethylorthosilcate as the reactive hydrophilic component. An organic photoinitiator and a crosslinking agent were co-dissolved in the organic regions of the liquid-crystalline phase in order to produce a highly crosslinked network upon photolysis. A water-soluble photoacid generator (2-hydroxy-2-methylpropiophenone) was dissolved in the hydrophilic channels in order to initiate acid-catalyzed silica condensation *in situ*.

Sodium *p*-styryloctadecenoate is a polymerizable styrene analog of lithium stearate, a molecule which is known to adopt the inverse hexagonal phase. The monomer is prepared as described in Example 1.

Initial phase characterization studies revealed that mixtures of sodium *p*-styryloctadecenoate containing small amounts of 1,4-divinylbenzene (ca. 5-10 wt %), 2-hydroxy-2-methylpropiophenone (an organic photoinitiator) (ca. 2 wt %), and pure water (2-20 wt %) form a well-defined inverse hexagonal phase, as confirmed by polarized light

microscopy and low angle x-ray diffraction. The optical textures of these mixtures are consistent with those of other hexagonal phases encountered in the literature. The low water content in these mixtures (≤ 20 wt %) indicates that they are indeed inverse mesophases. The hexagonal architecture in these samples was confirmed by low-angle x-ray diffraction, yielding, a characteristic spacing ratio of

$$1 : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{7}} : \frac{1}{\sqrt{9}} : \frac{1}{\sqrt{12}} \ldots .$$

Subsequent reagent compatibility studies demonstrated that sodium *p*-styryloctadecenoate also adopts the desired inverse hexagonal mesophase in the presence of TEOS solution. For example, a mixture containing 73 wt % 1; 15 wt % divinylbenzene; 2 wt % 2-hydroxy-2-methylpropiophenone; and 10 wt % of a solution containing 44.8% TEOS, 38.8% ethanol, 15.8% H_2O, and 0.6% diphenyliodonium chloride (a water-soluble photoacid), exhibits the characteristic optical texture and x-ray diffraction spacings of a hexagonal ensemble. The primary reflection yielded a d_{100} spacing of 35.4 Å, corresponding, to an interchannel distance of 40.9 Å. The unit cell dimensions of the inverse hexagonal phase, and thus the diameters of the hydrophilic channels, change only slightly when a hydrophilic TEOS solution is used in place of water for phase formation.

Photopolymerization of the lyotropic liquid-crystalline mixture containing, TEOS, as described above, proceeded with retention of phase architecture. The initial monomer mixture is a colorless, translucent, viscous mixture. After irradiation with 365 nm light (1800 $\mu W/CM^2$) under nitrogen for 24 h, the product is a tough, pale-yellow, clear, glassy material that is completely insoluble in common organic solvents and water. UV-visible analysis of the initial unpolymerized mixture showed absorptions centered at λ_{max} = 208 and 254 nm. After photolysis, the absorptions shift to 194 and 246 nm, respectively, with a marked decrease in the intensity of the second peak. IR spectra taken of samples before and after polymerization show the disappearance of olefinic bands at 1630, 989, and 902 cm^{-1}. These data are

consistent with the loss of the conjugated olefinic functionalities and a high degree of polymerization. Polarized light microscopy analysis of the mixture before and after photopolymerization revealed nearly identical optical textures. Similarly, x-ray diffraction analysis of the monomer mixture before and after photolysis revealed the same set of diffraction peaks with only a small change (4.0%) in unit cell dimensions and a reduction in intensity of the primary reflection. These data are consistent with preservation of the hexagonal nanoarchitecture upon network formation.

Sonication of a powdered nanocomposite sample with $CDCl_3$, CD_3OD, and D_2O, and subsequent ^1H NMR analysis of the extracts indicated that no residual free monomer, divinylbenzene, or TEOS remained. Thus both organic network formation and silica condensation occur upon photolysis at room temperature. ^{29}Si solid-state NMR spectroscopy was used to verify the extent of condensation of TEOS within the matrix (Figure 4a,4b). Silicon centers in silicates are typically designated Q^n, where *n* represents the number of adjoining, siloxy substituents, as opposed to hydroxy or alkoxy substituents. Strong resonances at -112 (41) and -100 (42) ppm relative to tetramethylsilane (TMS) and a weak resonance at -88 (43) ppm (Figure 4a) are characteristic of a highly crosslinked, photoacid-condensed silica network consisting, mostly of Q^4 and Q^3 silicon centers, with a small amount of Q^2 centers, respectively. Q^0 and Q^1 centers (45, 44) resonate closer to TMS. Although silica condensation is not complete after photolysis at room temperature, the predominance of the di- and trisiloxysilane peaks in the ^{29}Si NMR spectrum of the nanocomposite (Figure 4b) indicates that the encapsulated silica gel is also crosslinked to a high degree. This occurs without destruction of the order of the surrounding matrix. The degree of condensation can be further enhanced by heating the material under vacuum to drive off water. Thermogravimetric analysis (TGA) revealed that the onset of decomposition of the silica nanocomposite is 438°C (10°C/min ramp rate under nitrogen). The crosslinked polymer matrix

itself is thermally stable up to 429°C under the same conditions.

Small modifications in the structure of the amphiphilic monomer can be used to alter the unit cell dimensions of the matrix in a highly uniform fashion and, in some instances, change the geometry of the phase entirely. For example, a sample formed with sodium *p*-styryloctadecenoate, divinylbenzene, and water exhibits an inverse hexagonal phase with a primary diffraction peak at 35.4 Å; a sample formed with the corresponding potassium salt exhibits a complex lamellar phase with a primary reflection at 39.7 Å; and a sample formed with the calcium disalt analog exhibits an inverse hexagonal phase with a primary reflection at 30.9 Å.

3.2 Ordered Nanocomposites from Sodium 3,4,5-Tris(11'-acryloyloxyundecyloxy)benzoate as the matrix monomer and a PPV precursor solution as a channel filler

A hexagonally ordered nanocomposite containing PPV was formed by initially mixing an aqueous solution of the PPV precursor, poly(*p*-xylylenedimethylsulfonium chloride, prepared with monomer sodium 3,4,5-tris(11'-acryloyloxyundecyloxy)-benzoate and an organic radical photoinitiator (2-hydroxy-2-methylpropiophenone) to establish the desired inverse hexagonal liquid-crystalline phase. In order to generate the PPV nanocomposite, a 1 wt % aqueous solution of poly(*p*-xylylenedimethylsulfonium chloride) was used as the hydrophilic component in the formation of the phase. A mixture of 80 wt% sodium 3,4,5-tris(11'-acryloyloxyundecyloxy)benzoate, 10 wt% of the PPV precursor solution, and 10 wt% of a *p*-xylene solution containing 20% photoinitiator, was found to afford a well-defined, stable inverse hexagonal phase at ambient temperature. The optical texture of this mixture under the polarized light microscope is consistent with that of a lyotropic inverse hexagonal mesophase. The x-ray diffraction profile exhibits *d* spacings with ratios of $1 : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{7}} : \frac{1}{\sqrt{9}} : \frac{1}{\sqrt{12}} \ldots$ indicative of a hexagonal phase.

Polymerization with retention of phase architecture was

performed by irradiating the viscous liquid-crystalline monomer mixture with 365 nm light in air, either in the bulk or as thin films. The resulting material is a tough, pale yellow, translucent polymer resin that is insoluble in common solvents. The polymer exhibits an optical texture under crossed polarizers and an x-ray diffraction profile virtually identical to that of the liquid-crystalline monomer mixture. Figure 5a shows low angle x-ray diffraction profiles of a mixture containing 80 wt% 1, 10 wt% aqueous PPV precursor solution, and 10 wt% of a *p*-xylene solution containing 2-hydroxy-2-methylpropriophenone before photopolymerization and 5(b) shows the mixture after photopolymerization. The unit cell dimensions in the photopolymerized material are slightly smaller, consistent with a slight volume contraction upon network formation. A high degree of crosslinking occurs upon photolysis, as confirmed by the almost complete disappearance of the acrylate bands at 1635, 985, and 810 cm^{-1} in the FT-IR spectrum of the photolyzed material. Extraction of the polymer with deuterated solvents and subsequent ^{1}H NMR analysis of the extracts also did not reveal any residual free monomer. The hexagonal nanoarchitecture was confirmed unequivocally by transmission electron microscopy (TEM). The photopolymerized material consists of a regular, hexagonal array of channels approximately 40 Å in diameter, and is in excellent agreement with the x-ray diffraction results. The PPV precursor is believed to reside solely in the aqueous channels of the liquid-crystalline monomer phase and the resulting polymerized network because the precursor is a highly charged polyelectrolyte that is completely insoluble in nonpolar media.

Conversion of the PPV precursor in the nanocomposite proceeds partially during photolysis of the liquid-crystalline monomer mixture but the reaction can be accelerated by thermal treatment. The concentration of PPV (<0.1 wt %) in the composite is well below the detection limit of many characterization techniques such as UV-visible, solid-state ^{13}C NMR, FT-IR, and Raman spectroscopy; however, the degree of PPV conversion can be monitored qualitatively by fluorescence

spectroscopy. A typical PPV nanocomposite film photopolymerized at ambient temperature exhibits intense fluorescence at 504 and 534 nm when excited with 370 nm light, even though the electronic absorptions of the PPV segments in the composite are too weak to be observed by UV-visible spectroscopy. In comparison, poly(*p*-xylylenedimethylsulfonium chloride) exhibits only very weak fluorescence under the same conditions (due to a small amount of spontaneous conversion at room temperature), whereas pure PPV prepared by heating the precursor at 220 °C *in vacuo* exhibits relatively strong fluorescence at 517 and 547 nm. When the nanocomposite is subjected to the same thermal treatment to drive the PPV conversion process, its fluorescence intensity at first increases dramatically as a function of heating time. This behavior is consistent with an increase in the number of emitting PPV segments as a higher degree of conversion is achieved. The wavelengths of emission remain essentially unchanged during the conversion process. After 4 h at 220 °C, the ordered nanocomposite, which contains less than 0.1 wt % PPV, emits approximately 2.0 times more light *per unit volume* than *pure* PPV over the 400-700 nm range. This ratio translates into a very large photoluminescence enhancement based on the amount of PPV in the two samples.

Photoluminescence enhancement in conjugated polymers has been reported for polymers that can be dissolved in solution or interchain-separated in amorphous composites and copolymers to minimize self-quenching mechanisms. While dilution of the PPV segments or chains may be responsible for part of the enhanced fluorescence in the present nanocomposite, the nanometer-scale order of the system also plays a role as a dramatic reduction in fluorescence intensity occurs when the order in the composite is degraded after 20 h at 220°C. Thermogravimetric analysis of the nanocomposite indicated that only a 3% weight loss occurs after this heating period. Thus, the fluorescence enhancement cannot be due entirely to a simple dilution effect because the effective concentration of PPV in the composite is not significantly affected by the heating process. Thermal decomposition of the PPV or the

matrix also cannot account for this behavior because PPV is thermally stable up to 570°C under inert atmosphere, and IR analysis of composite did not reveal any significant chemical changes during the heating, except for the loss of residual acrylate groups.

The differences in the fluorescence spectra and the emission behavior of the present nanocomposite and pure PPV indicate that the ordered, ionic channels of the matrix represent a substantially different local environment for PPV.

EXAMPLE 4

This example illustrate the formation of nanocomposites which are thin films and fibers.

In terms of processing, the nanocomposite can be easily fabricated into highly aligned free-standing thin films and fibers. Thin films several square centimeters in area with the aqueous channels almost uniformly aligned perpendicular to the film surfaces were produced by heating the monomer mixture into a fluid, isotropic state between glass slides, pressing the fluid into a film, and allowing the mixture to slowly cool between the plates before photopolymerization. The films are almost uniformly dark under crossed polarizers but appear bright around areas of applied stress. When ground up, the films exhibit the x-ray diffraction pattern for a hexagonal phase which is consistent with overall homeotropic alignment.

Highly anisotropic fibers can be obtained by extruding the viscous monomer mixture through a syringe needle and photopolymerizing the resulting fiber.

EXAMPLE 5

This example illustrates the use of a nanoporous polymer network as a catalyst in the Knoevenagel reaction.

A well-defined inverse hexagonal phase was formed with the addition of H_2O, the cross-linker divinylbenzene, and the photoinitiator 2-hydroxy-2-methylpropiophenone to monomer **1** in Scheme I with subsequent mixing. Low-angle x-ray diffraction revealed characteristic *d*-spacing ratios of $1 : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{7}} : \frac{1}{\sqrt{9}} : \frac{1}{\sqrt{12}} \ldots$. The matrix was found to have an interchannel distance of about 40 Å. Radical photopolymerization locked the liquid crystal phase into place, forming a network with well-defined channels. X-ray diffraction analysis after polymerization revealed that the matrix had retained the inverse hexagonal phase. The matrix was then crushed by mortar and pestle to a powder on the micrometer range to increase surface area for use in the

catalytic studies.

Both zeolites and mesoporous molecular sieves have been advanced as useful catalysts for accomplishing the condensation. To determine whether the unique structural features of the instant liquid crystal network played a role in catalyzing the condensation, control experiments with sodium acetate were carried out. By using free carboxylate groups in solution, it would be determined if the increased reactivity was due merely to the presence of carboxylate groups or if the physical proximity of carboxylates had a catalytic effect. Aliquots were taken every half hour for the first three hours, then after 4 h and after 7h. Reactions with the liquid crystal network were monitored by GC using dodecane as the standard. The reactions with sodium acetate and sodium oleate were monitored by ^{1}H NMR spectroscopy. The reactions with sodium acetate were monitored by ^{1}H NMR spectroscopy, using *p*-xylene as the internal standard. The reactions monitored by NMR spectroscopy were carried out in THF-d_8. As the solvent is not involved in bond breaking, there should be no kinetic isotope effect.

The reaction of benzaldehyde and ethyl cyanoacetate in THF with the liquid crystal network at 30°C showed minimal conversion to product even after 7 h. Therefore, the reactions were carried out in refluxing THF (67°C) to speed the rate of the reaction. With no base added, the reaction predictably showed no conversion to product in THF after 24 h. However, the reaction with the liquid crystal network did proceed and was repeated three times to confirm its reproducibility. The three runs were monitored by the disappearance of ethyl cyanoacetate. The reaction was monitored by the disappearance of both reactants as well as the appearance of the product. While the disappearance of the two reactants appeared to occur at a similar rate, the appearance of the product was observed to occur at a slower rate and at a lower percent conversion after 7 h.

Reactions were then carried out with sodium acetate. It was shown that sodium acetate acting as free carboxylates in solution were less effective in causing the reaction to

proceed. The rate was considerably slower.

As the system is a heterogeneous one, factors affecting the rate of diffusion must be taken into consideration. In particular, the stirring rate and particle size can affect the rate of diffusion. The reaction with the liquid crystal network was carried out at different stirring rates. Results indicate that stirring rate does affect the rate of reaction, the slower stirring rate facilitating the conversion to more product.

The liquid crystal network was typically crushed with mortar and pestle, and a mixture of particle sizes used for the reactions involving the liquid crystal network. However, in order to study the effect of particle size, the liquid crystal network was separated into two fractions using a No. 200 mesh. One fraction contained particle sizes greater than 75 mm and the other particle sizes smaller than 75 mm. Smaller particle size exhibited a faster initial rate. This result may be due to the fact that increased surface area will expose more pore openings, allowing more sites at which the reactants can enter the pores.

These studies indicate that stirring rate and particle size do indeed have an effect on the rate. These differences confirm that the instant invention involves a heterogeneous system with the problems commonly associated with these kinds of systems. Thus, demonstrating the catalytic activity of the liquid crystal network.

Preparation of liquid crystal phases: Liquid crystal monomer samples were prepared by combining the monomer **7** (*see* Example 1.7) (1.08 g, 84 wt %), the initiator 2-hydroxy-2-methyl propiophenone (0.0256 g, 2 wt %), divinylbenzene (0.0769 g, 6 wt %), and Optima grade H_2O (0.111 g, 8 wt %) in a 40-mL centrifuge tube. The sample was alternately sonicated for 15 min and centrifuged for 20 min at 2300 rpm. This procedure was repeated twice. The sample was then allowed to stand overnight at room temperature. The phase was confirmed by powder X-ray crystallography and shown to have characteristic hexagonal spacings: 37.05, 21.42, 19.04, 14.06, 12.39, 10.39 Å.

Photopolymerization: Photopolymerizations were carried out under a N_2 flush for 12 h at room temperature using a Cole-Parmer 9815 series 6 watt UV (365 nm) lamp. liquid crystal samples were smeared on quarts slides and placed into a quartz tube under N_2 pressure. Initial conversion of the liquid crystal monomer mixture to a glassy cross-linked network occurs within the first hour of irradiation.

Typical catalysis study for GC. Ethyl cyanoacetate (0.254 mL, 2.50 mmol), benzaldehyde (0.266 mL, 2.50 mmol), and dodecane (0.142 mL, 0.625 mmol) were added to THF (5 mL). The reaction was placed in an oil bath at 67°C. To the stirring reaction mixture, 5 mol % of the liquid crystal network was added. The reactants were added in air but an atmosphere of N_2 was applied for the duration of the reaction. Aliquots were taken every half hour for the first 3 h, after 4h, and after 7 h. Aliquots were placed in the centrifuge for 1.5 min at 2500 rpm. The supernatant was filtered through a glass fiber plug. 8 μL of this solution was dissolved in 200 μL of THF. These sample was then stored in the refrigerator before ejecting into the GC.

Typical catalysis study for ^{1}H NMR. Ethyl cyanoacetate (0.133 mL, 1.25 mmol), benzaldehyde (0.127 mL, 1.25 mmol), and *p*-xylene (0.0766 mL, 0.625 mmol) were added to THF-d_8. The reaction was placed in an oil bath at 67°C. To the stirring reaction mixture, 5 mol % of sodium acetate or sodium oleate was added. The reactants were added in air but an atmosphere of N_2 was applied for the duration of the reaction. Aliquots were taken every half hour for the first 3 h, after 4h, and after 7 h. The aliquot was filtered through a glass plug and diluted with additional THF-d_8. Samples were stored in the refrigerator until data was collected on the spectrometer.

EXAMPLE 6

This example shows in situ polymerization of the lyotropic liquid crystal monomer with retention of phase microstructure.

A bulk sample of **1** of Scheme I containing 10 wt % divinylbenzene, 8 wt % H_2O, and 2 wt % organic photoinitiator,

2-hydroxy-2-methylpropiophenone, still exhibits the inverse hexagonal phase as determined by polarized light microscopy and low angle x-ray diffraction. When a thin film of this colorless, translucent, viscous liquid crystal mixture was placed on a quartz slide and irradiated with a long wavelength UV lamp (l_{max} = 365 nm) for 4 h at room temperature, the resulting product was an tough, colorless clear, glassy material that was completely insoluble in common organic solvents and water. Extraction of this polymer with $CDCl_3$ and subsequent ^1H NMR analysis of the extracts revealed that no residual free monomer or divinylbenzene remained. This implies that network formation was essentially complete. Comparison of the optical textures of the material under the polarizing microscope before and after photopolymerization showed the same texture, thus indicating that no appreciable change in phase microstructure had occurred upon crosslinking. This fact was confirmed by x-ray diffraction analysis of the sample before and after photolysis. The x-ray diffraction profile of the crosslinked network is consistent with an inverse hexagonal mesophase and is essentially identical to that of the initial monomer mixture. The individual *d* spacings are all slightly smaller in the network due to the slight volume contraction expected upon crosslinking. UV-visible analysis of the initial monomer mixture showed four overlapping absorptions at centered at 210, 236, 264, and 294 nm. After photolysis, the absorption at l_{max} = 294 nm was absent in the polymer network. This is consistent with the loss of the conjugated units (*i.e.*, divinylbenzene and the styrene groups) upon polymerization.

EXAMPLE 7

This example shows uniform alignment in the nanoporous polymer membrane.

When a mixture of **1'** of Scheme II containing 10 wt % water, and 10 wt % of a *p*-xylene solution containing 20 wt % 2-hydroxy-2-methylpropriophenone is placed between two microscope slides and heated momentarily, the mixture turns from a viscous gel to a very fluid isotropic melt. It is

possible to press the melt into very thin transparent films between the glass slides at this stage. After slow cooling to room temperature, the thin film appears almost uniformly dark under crossed polarizers. Subsequent photopolymerization of the film yielded a robust, thin, colorless, transparent film that could be peeled off the glass slides in one piece. The polymerized film exhibited the same essentially uniformly dark texture; however, when the film was ground up and analyzed by x-ray diffraction, the expected hexagonal diffraction pattern was still observed. This data is consistent with the hexagonally arranged pore channels being uniformly aligned perpendicular to the surface of the glass slides (*i.e.*, homeotropically aligned).

EXAMPLE 8

This example describes preparation of a transition metal salt of **1** of scheme I.

Procedure 1

To a 200 mL round-bottomed flask with magnetic stirring bar, 1.0 g compound **1** was added, following by addition of 100 mL acetone and 10 mL methanol. The solution was titrated by NaOH aqueous solution to PH = 7. After 30 minutes stirring, 0.17 g Co (II) nitrate hexahydrous was added slowly into the solution. The reaction was allowed to run for 2 hrs. The solvent was removed by vacuum. The solid was washed by 3 x 20 mL distilled water. The residue was resolved in 20 mL acetone. The solution was filtered and solvent removed by vacuum. Another 20 mL acetone was injected into the flask and then pumped out. The resulting solid was dried by vacuum over night. A green solid was obtained with about 80 % yield.

Procedure 2

To a 200 mL round-bottomed flask with a magnetic stirring bar, 1.0 g compound **1**, 100 mL acetone and 10 mL MeOH were added, following by the addition of 0.17 g Co(II) nitrate hexahydrous solution in acetone. The solution was then

titrated to PH = 7 slowly with 10 % NaOH aqueous solution. The reaction was allowed to stand for 2~3 hours. Solvent was then removed by vacuum and the solid residence was washed by 3x20 mL distilled water. In order to dry the salt, the residue was resolved in 50 mL acetone and then pumped out. The procedure was repeated twice and the resulting residue was dried by vacuum over night. A green solid was obtained in a yield of 80 %.

Preparation of liquid crystal phase of monomer **1** of Scheme I:

20 % photoinitiator solution was prepared by dissolving the 2-hydroxy -2-methyl propiophenone (2.0 g) in degassed p-xylene (8.0 g). In order to make a inversed hexagonal phase, 0.85 g monomer **1**, 0.10 g distilled water and 0.05 g photoinitiator xylene solution were added into a 40 mL centrifuge tube under nitrogen atmosphere. The resulting mixture was centrifuged at 2800 rpm for 12 min., hand-mixed with a spatula and then placed in a ultrasonic bath for 10 min. The above procedure was repeated twice until a homogeneous phase was observed and identified by polarized light microscope and x-ray diffraction pattern.

Preparation of a film using the liquid crystal above:

The liquid crystal (LC) material (0.15g) was put onto a quartz flat lens (3' dia) with a Teflon spatula, which was covered by another piece of the flat lens to make a sandwich. In order to obtain uniform thickness, several strips of a $5.0x10^{-5}$ m feeler gauge were placed between the lenses. The sandwich was put into a 90 °C oven for 20 min until the liquid crystal melted into anisotropic liquid. Once a homogeneous liquid was observed, the sandwich was removed and placed into a polycarbonate pressure clamp. By tightening the four screws on the clamp, a thin film was formed between the lenses. After the system was cooled down to room temperature, the sandwich was exposed to a 6 watt, 365 nm UV lamp placed on directly on top of the sandwich for 12 hours in nitrogen filled glovebag. Another hour of irradiation of the UV was exerted after the clamp was removed. Finally, the sandwich was placed into a water bath to lift the film off the lens and

then air and vacuum dried.

Example procedure for transition-metal and lanthanide salt formation of monomer **1'** in Scheme II:

In a 50 mL Erlenmeyer flask, 0.5000 g (1.293 mmol) of p-styryloctadecanoic acid was dispersed in 20 mL of absolute ethanol. Separately, a 0.155 M aqueous solution of sodium hydroxide was prepared by dissolving 0.6207 g of sodium hydroxide in 100.0 mL of deionized water. To the acid mixture was added 8.4 mL (1.3 mmol) of the NaOH solution slowly with stirring. After a few seconds of bubbling and cloudiness, the solution turned clear. Separately, 0.1882 g (1.293 mmol) of cobalt (II) chloride hexahydrate was dissolved in 10 mL absolute ethanol and 10 mL water in a 250 mL Erlenmeyer flask. The solution turned pale brown in color. To this solution was added the above ethanolic salt solution dropwise with vigorous stirring. As the addition proceeded, the solution turned cloudy, and deep purple specks began to form. After the addition was complete, the solution mixture was heated gently for five minutes, and then allowed to cool. To the mixture was poured into a separatory funnel with 30 mL of pentane and shaken vigorously. The mixture separated into two distinct layers: the bottom, clear, aqueous layer, and the top, purple, organic layer. The organic layer was separated, and the aqueous layer was additionally extracted twice with 20 mL of pentane. The combined organic layers were washed with 50 mL of saturated aqueous NaCl solution and 50 mL of deionized water, and dried over sodium sulfate. The solvents were removed in vacuo, yielding a sticky, dark purple product. Elemental analysis confirmed the composition of the product.

Variation for other salts:

The above procedure is applicable to a wide selection of transition-metals and lanthanides. In each case, the appropriate quantity of the transition metal chloride or nitrate was used. The colors of the solutions and consistency of the products vary greatly depending on the identity of the transition metal used. Cobalt (II), manganese (II), cadmium

(II), nickel (II), iron (III), copper (II), europium (III), and cerium (III) salts have been prepared and characterized. Chromium (III) and lanthanum (III) salts have been prepared, but not yet characterized. Non-transition metal salts - calcium, potassium, cesium - have been prepared and partially characterized, and other salts - barium and gallium - have been prepared but not yet characterized.

The above description is illustrative and not restrictive. Many variations of the invention will become apparent to those of skill in the art upon review of this disclosure. The scope of the invention should, therefore, be determined not with reference to the above description, but instead should be determined with reference to the appended claims along with their full scope of equivalents.

WHAT IS CLAIMED IS:

1. An ordered nanocomposite of a matrix component and a filler component, said matrix comprising polymerized inverse hexagonal-forming lyotropic liquid-crystalline monomers and defining a hexagonally-packed array of tubular channels, said filler component being present in said tubular channels.

2. A nanocomposite in accordance with claim 1, wherein said inverse hexagonal-forming lyotropic liquid-crystalline monomers have a critical packing parameter of greater than 2.

3. A nanocomposite in accordance with claim 1, wherein said matrix comprises polymerized inverse hexagonal-forming lyotropic liquid-crystalline monomers which have been polymerized in the presence of a crosslinker.

4. A nanocomposite in accordance with claim 1, wherein said monomers have a hydrophophilic head group and a branched hydrophobic tail group, said hydrophilic head group being a member selected from the group consisting of a carboxylate salt, a phosphonate salt, a phosphate salt, a sulfate salt, a sulfonate salt, a sulfonium group, and an ammonium salt, wherein said tail group contains a polymerized group.

5. A nanocomposite in accordance with claim 4, wherein said polymerized group is present in said monomer prior to said polymerization as a member selected from the group consisting of an acrylate, a styrene, a vinyl ester, a 1,3-diene and an acrylamide.

6. A nanocomposite in accordance with claim 1, wherein said filler component is an organic polymer.

7. A nanocomposite in accordance with claim 6,

wherein said second organic polymer is a conjugated polymer selected from the group consisting of photoluminescent polymers and electroactive polymers.

8. A nanocomposite in accordance with claim 1, wherein said nanocomposite is formed into a fiber.

9. A nanocomposite in accordance with claim 1, wherein said nanocomposite is formed into a film.

10. A nanocomposite in accordance with claim 1, wherein said filler component is an inorganic material selected from the group consisting of magnetic ceramic particles, semiconductors, metal particles, alumina, silica, and metal salts.

11. A nanocomposite in accordance with claim 1, wherein said monomers, in an unpolymerized form, have the formula:

$HG^1-T-(X^1-PG^1)_n$ **(I)**

wherein

HG^1 represents a hydrophilic head group;

T represents a bond or a template for the attachment of lipid tail groups, said template being selected from the group consisting of aromatic rings, monosaccharides, and polyhydroxylated lower alkyl groups;

each X^1 independently represents a lipid tail group having from 8 to 24 carbon atom in a linear or branched chain and optionally interrupted by one or more heteroatom groups selected from the group consisting of —O—, —NH—, —NR—, and —S— wherein R is a lower alkyl or lower acyl group;

each PG^1 is a polymerizable group; and

n is an integer of from 1 to 4.

12. A nanocomposite in accordance with claim 11, wherein T is a phenyl ring and n is from 2 to 4.

13. A nanocomposite in accordance with claim 11,

wherein HG^1 is a carboxylic acid salt, T is a phenyl ring, n is from 2 to 3, and each PG^1 is an acrylate group.

14. A nanocomposite in accordance with claim 11, wherein HG^1 is a carboxylic acid salt, T is a bond, n is 1, PG^1 is styryl group, and X^1 is a branched chain alkyl group having from 12 to 24 carbon atoms.

15. A nanocomposite in accordance with claim 11, wherein HG^1 is a carboxylic acid salt, T is a bond, n is 1, PG^1 is styryl group, X^1 is a straight chain alkyl group having from 12 to 24 carbon atoms, and PG^1 is attached to X^1 at a non-terminus position.

16. A method of forming an ordered nanocomposite comprising a matrix component of polymerized inverse hexagonal-forming lyotropic liquid-crystalline monomers and having hexagonally-packed tubular channels, said method comprising:

(a) combining a quantity of polymerizable inverse hexagonal-forming monomers, an aqueous or polar organic solvent, and channel filler precursor materials to form a pre-polymer mixture in which said polymerizable monomers adopt an inverse hexagonal phase around said aqueous or polar organic solution; and

(b) polymerizing said pre-polymer mixture to form said nanocomposite matrix component having hexagonally-packed tubular channels.

17. A method in accordance with claim 16, wherein said polymerizing is initiated by ultraviolet light or heat.

18. A method in accordance with claim 16, wherein said polymerizing is initiated by a radical initiator.

19. A method in accordance with claim 16, wherein said pre-polymer mixture further comprises a crosslinker.

20. A method in accordance with claim 16, wherein said aqueous or polar organic solution further comprises inorganic precursors to solid state materials.

21. A method in accordance with claim 16, wherein said aqueous or polar organic solution further comprises a sol-gel silica precursor solution.

22. A method in accordance with claim 21, wherein said matrix is an ordered polymer-inorganic nanocomposite, said method further comprising:

(c) polymerizing said sol-gel silica precursor solution.

23. A method in accordance with claim 16, wherein said aqueous or polar organic solution further comprises a conjugated organic, photoluminescent polymer precursor.

24. A method in accordance with claim 23, further comprising:

(c) converting said precursor to a conjugated organic, photoluminescent polymer.

25. A method in accordance with claim 16, wherein prior to said polymerizing, said pre-polymer mixture is formed into a thin film.

26. A method in accordance with claim 16, wherein prior to said polymerizing, said pre-polymer mixture is extruded into a fiber.

27. A method in accordance with claim 16, wherein said channels have a diameter of from about 2 to about 6 nanometers.

28. A matrix having an ordered array of hexagonally spaced tubular channels formed by the polymerization of inverse hexagonal phase-forming monomers, said channels having

a diameter of from about 2 to about 6 nanometers.

29. A nanocomposite formed by the method of claim 16.

30. An inverse hexagonal phase-forming lyotropic liquid-crystalline compound having the formula:

$HG^1-T-(X^1-PG^1)_n$ **(I)** wherein

HG^1 represents a hydrophilic head group;

T represents a bond or a template for the attachment of lipid tail groups, said template being selected from the group consisting of aromatic rings, monosaccharides, and polyhydroxylated lower alkyl groups;

each X^1 independently represents a lipid tail group having from 8 to 24 carbon atom in a linear or branched chain and optionally interrupted by one or more heteroatom groups selected from the group consisting of —O—, —NH—, —NR—, and —S— wherein R is a lower alkyl or lower acyl group;

each PG^1 is a polymerizable group; and

n is an integer of from 1 to 4.

31. A compound in accordance with claim 30, wherein T is a phenyl ring and n is from 2 to 4.

32. A compound in accordance with claim 30, wherein HG^1 is a carboxylic acid salt, T is a phenyl ring, n is from 2 to 3, and each PG^1 is an acrylate group.

33. A compound in accordance with claim 30, wherein HG^1 is a carboxylic acid salt, T is a bond, n is 1, PG^1 is styryl group, and X^1 is a branched chain alkyl group having from 12 to 24 carbon atoms.

34. A compound in accordance with claim 30, wherein HG^1 is a carboxylic acid salt, T is a bond, n is 1, PG^1 is styryl group, X^1 is a straight chain alkyl group having from 12 to 24 carbon atoms, and PG^1 is attached to X^1 at a non-terminus position.

35. A nanoporous polymer comprising polymerized inverse hexagonal phase-forming lyotropic liquid-crystalline monomers defining a hexagonally-packed array of tubular channels.

36. A nanoporous polymer in accordance with claim 35, wherein said inverse hexagonal-forming lyotropic liquid-crystalline monomers have a critical packing parameter of greater than 2.

37. A nanoporous polymer in accordance with claim 35, wherein said polymer comprises polymerized inverse hexagonal-forming lyotropic liquid-crystalline monomers which have been polymerized in the presence of a crosslinker.

38. A nanoporous polymer in accordance with claim 37, wherein said crosslinker is divinylbenzene.

39. A nanoporous polymer in accordance with claim 35, wherein said monomers have a hydrophilic head group and a branched hydrophobic tail group, said hydrophilic head group being a metal salt and wherein said tail group contains a polymerized group.

40. A nanoporous polymer in accordance with claim 39, wherein said metal is a member of the group selected from cobalt, manganese, cadmium, nickel, iron, copper, europium, cerium, chromium, lanthanum, calcium, potassium, sodium, cesium, barium and gallium.

41. A nanoporous polymer in accordance with claim 35, wherein said monomers have a hydrophilic head group and a branched hydrophobic tail group, said hydrophilic head group being a member selected from the group consisting of a carboxylate salt, a phosphonate salt, a phosphate salt, a sulfate salt, a sulfonate salt, a sulfonium group, and an ammonium salt, wherein said tail group contains a polymerized group.

42. A nanoporous polymer in accordance with claim 35, wherein said polymerized group is present in said monomer prior to said polymerization as a member selected from the group consisting of an acrylate, a styrene, a vinyl ester, a 1,3-diene and an acrylamide.

43. A nanoporous polymer in accordance with claim 35, wherein said nanoporous polymer is formed into a membrane.

44. A nanoporous polymer in accordance with claim 35, wherein said nanoporous polymer is formed into a fiber.

45. A nanoporous polymer in accordance with claim 35, wherein said nanoporous polymer is formed into a crystal-type solid.

46. A nanoporous polymer in accordance with claim 35, wherein said monomers, in an unpolymerized form, have the formula:

$$HG^1T(X^1PG^1)_n \quad \textbf{(I)}$$

wherein

HG^1 represents a hydrophilic head group;

T represents a bond or a template for the attachment of lipid tail groups, said template being selected from the group consisting of aromatic rings, monosaccharides, and polyhydroxylated lower alkyl groups;

each X^1 independently represents a lipid tail group having from 8 to 24 carbon atom in a linear or branched chain and optionally interrupted by one or more heteroatom groups selected from the group consisting of O, NH, NR, and S wherein R is a lower alkyl or lower acyl group;

each PG^1 is a polymerizable group; and
n is an integer of from 1 to 4.

47. A method of forming a nanoporous polymer comprising a polymerized inverse hexagonal-forming lyotropic liquid-crystalline monomers and having hexagonally-packed tubular channels, said method comprising:

a) combining a quantity of polymerizable inverse hexagonal-forming monomers and an aqueous or polar organic solvent, to form a pre-polymer mixture in which said polymerizable monomers adopt an inverse hexagonal phase around said aqueous or polar organic solution; and

(b) polymerizing said pre-polymer mixture to form said nanoporous polymer.

48. A method in accordance with claim 47, wherein said polymerizing is initiated by ultraviolet light or heat.

49. A method in accordance with claim 47, wherein said polymerizing is initiated by a radical initiator.

50. A method in accordance with claim 47, wherein said pre-polymer mixture further comprises a crosslinker.

51. A method of catalyzing a chemical reaction comprising conducting said reaction in the presence of a nanoporous polymer, said polymer comprising polymerized inverse hexagonal phase-forming lyotropic liquid-crystalline monomers defining a hexagonally-packed array of tubular channels.

52. A method in accordance with claim 51, wherein said nanoporous polymer acts as a heterogeneous base catalyst.

53. A method in accordance with claim 51, wherein said nanoporous polymer acts as an acid.

54. A process of purifying water comprising contacting said solvent with a nanoporous polymer said polymer comprising polymerized inverse hexagonal phase-forming lyotropic liquid-crystalline monomers defining a hexagonally-packed array of tubular channels.

55. A method of separating a mixture comprising contacting said mixture with a nanoporous polymer said polymer comprising polymerized inverse hexagonal phase-forming lyotropic liquid-crystalline monomers defining a hexagonally-packed array of tubular channels.

56. A method of separating a mixture in accordance with claim 55 wherein said mixture is liquid.

57. A method of separating a mixture in accordance with claim 55 wherein said mixture is gaseous.

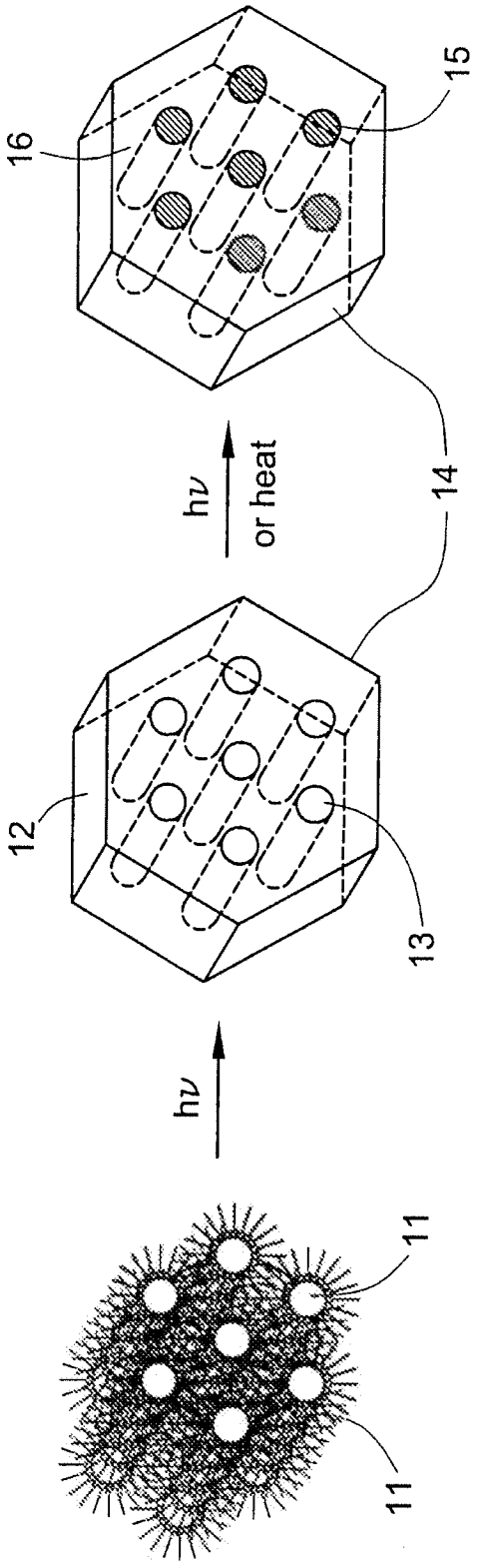

Fig. 1

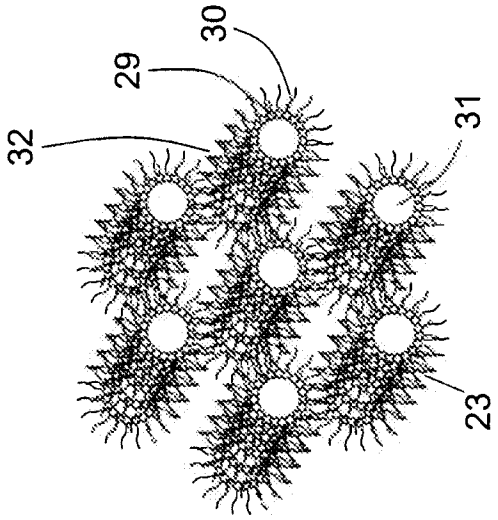

Fig. 2c

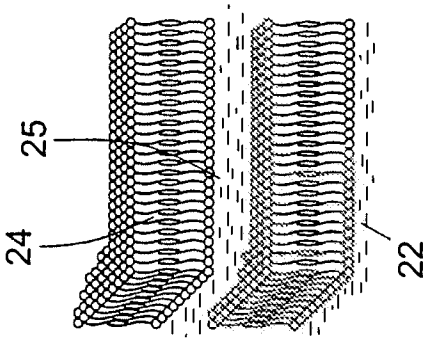

Fig. 2b

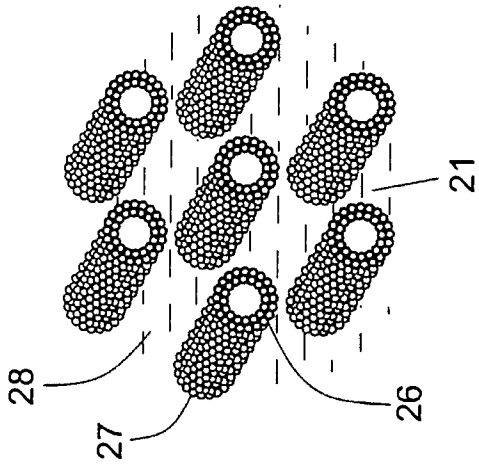

Fig. 2a

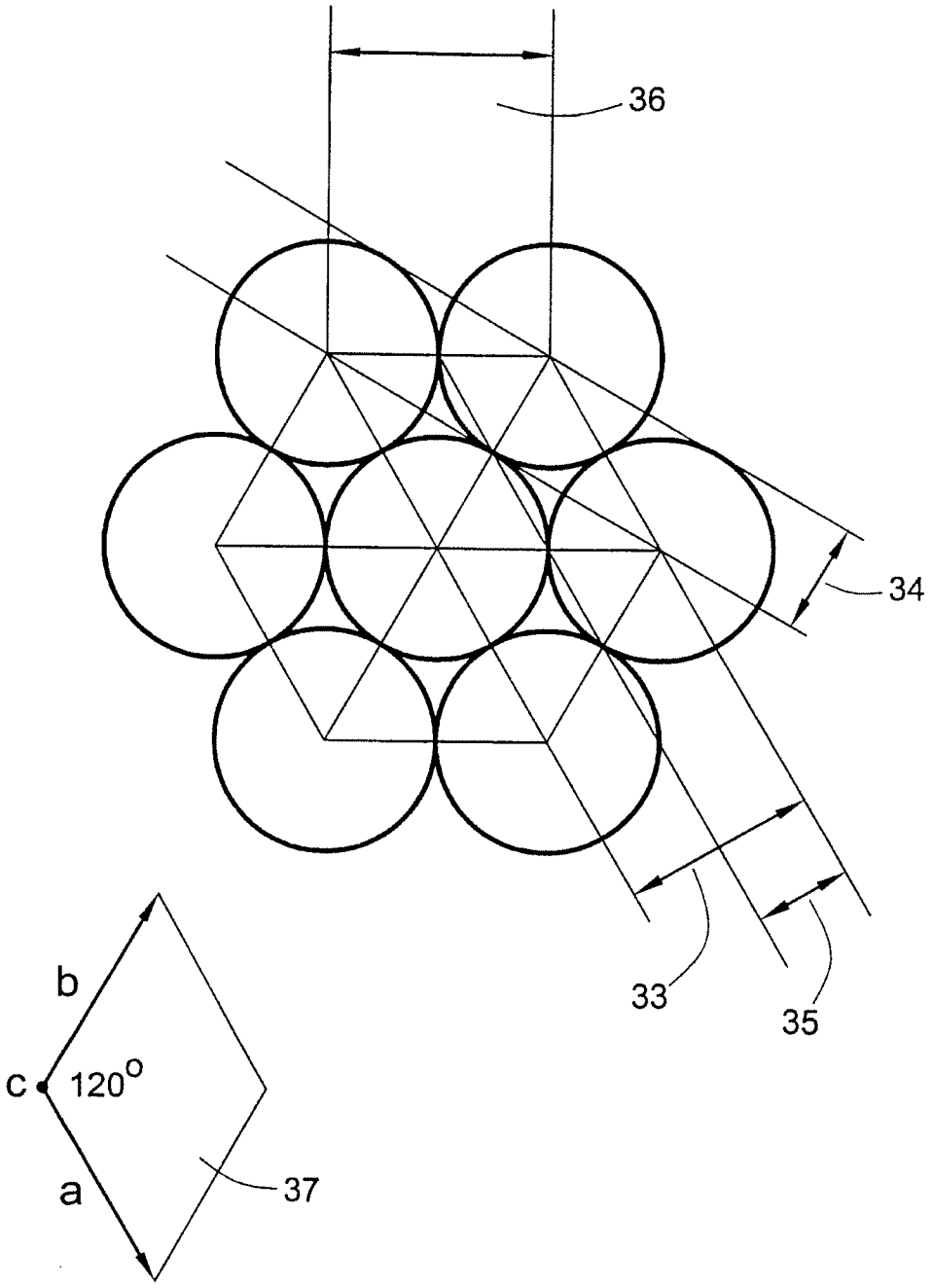

Fig. 3

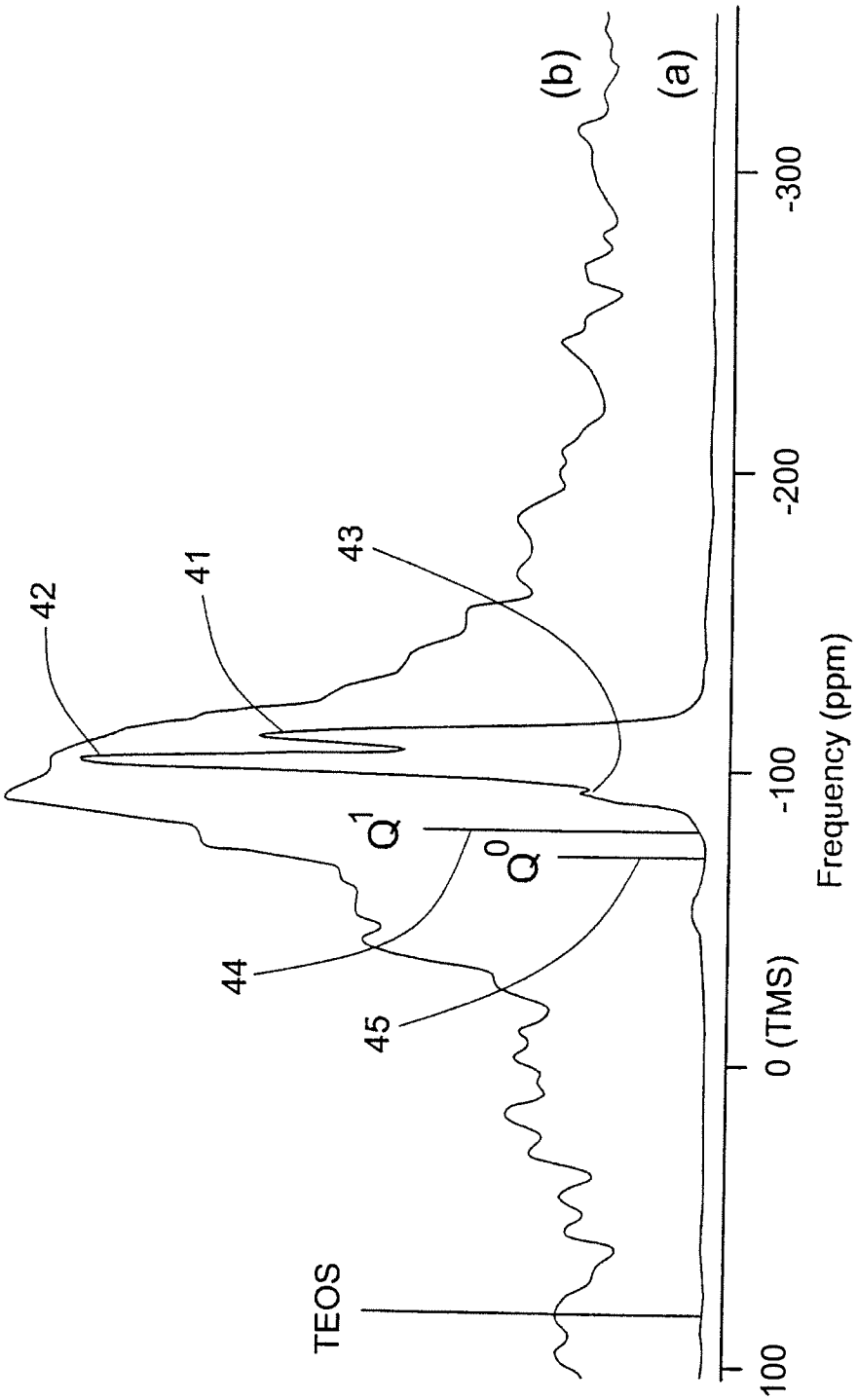

Fig. 4

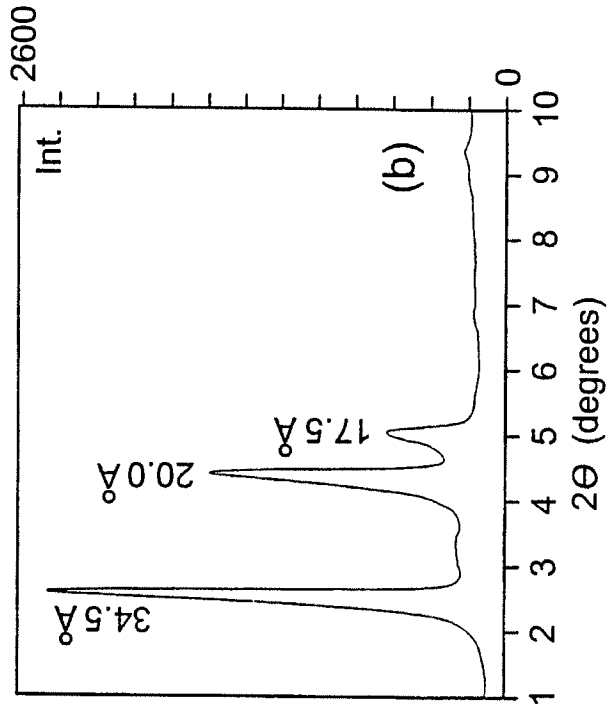
2600
Int.
(b)
0
1 2 3 4 5 6 7 8 9 10
2θ (degrees)
34.5Å
20.0Å
17.5Å

Fig. 5b

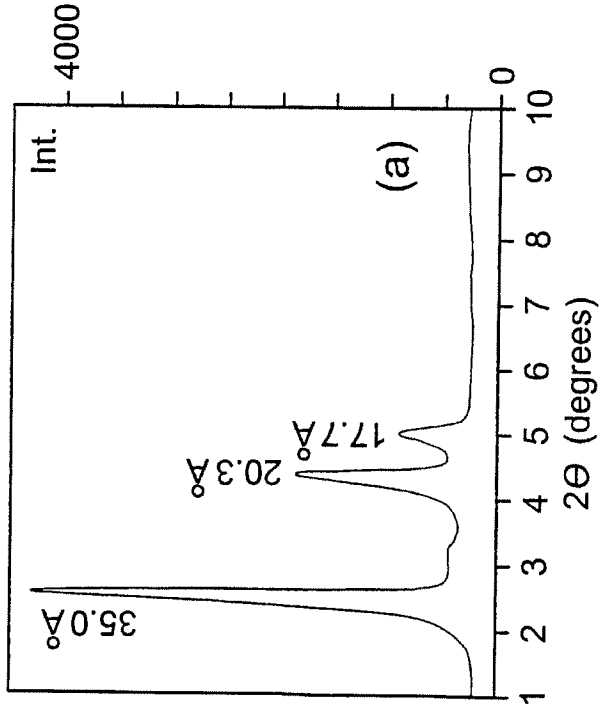
4000
Int.
(a)
0
1 2 3 4 5 6 7 8 9 10
2θ (degrees)
35.0Å
20.3Å
17.7Å

Fig. 5a